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Lead isotopic analyses of selected soil samples from the USEPA Vasquez Blvd.-I-70 study area, Denver, Colorado

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Introduction

Large amounts of arsenic contamination, in excess of 2000 ppm, have been found in some residential surface soils in northern Denver, Colorado (USEPA, 1999). Associated with the arsenic are elevated levels of metals such as lead, cadmium and mercury. Potential sources of this contamination include waste from smelters in the area and commercial herbicide containing arsenic trioxide and lead arsenate (USEPA, 1999). As a part of the U.S. Environmental Protection Agency's Vasquez Boulevard-I-70 Project (VBI70 project; USEPA, 1999), lead isotopic analyses of selected soil samples, smelter waste, and a commercial herbicide and a commercial lead arsenate pesticide have been performed in order to constrain the possible sources of elevated lead, and by proxy arsenic, found in these residential soils.

The isotopes of lead can be used as a natural tracer in determining sources of contaminants in soils and stream sediments (e.g. Church and others, 1997; Fey and others, 1999; Unruh and others, 2000). The element lead (Pb) consists of four naturally occurring and stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Three of these, ^{206}Pb, ^{207}Pb, and ^{208}Pb are radiogenic decay products of naturally occurring ^{238}U, ^{235}U, and ^{232}Th, respectively. Owing to variations among the U/Pb and Th/Pb elemental abundance ratios among different types of geologic materials, variations in the relative abundances of the Pb isotopes are produced among different materials during geologic time.

In order for the Pb isotope method to be useful for determining possible contaminant sources, two important criteria must be met (e.g. Church and others 1997): (1) It must be possible to obtain and measure the Pb isotopic compositions in all potential contaminant sources and in uncontaminated material and (2) the Pb isotopic compositions of the potential contaminant sources must be distinctly different from one another and from uncontaminated background. Variations among the Pb isotopic ratios in selected samples can be correlated with potential sources of Pb with known isotopic compositions in order to determine the relative contribution of Pb from a specific source to the sample.

The purpose of this study is to use Pb isotopic data obtained from a selected subset of samples to determine the Pb isotopic signatures of uncontaminated soils as well as those of potential sources of contamination. The data will eventually be used in conjunction with other geochemical data to help determine which source or sources of contamination are most likely responsible for the elevated arsenic levels in the residential soils.

Analytical Procedures

Chemical Procedures

Lead isotopic analyses of natural materials are obtained using anion-exchange, solid-liquid chromatography and thermal-ionization solid-source mass spectrometry. Samples were received as sieved soils from USEPA. Samples were digested in nitric acid and hydrogen peroxide in accordance with Section 7.2 of method 3050B, EPA SW 846, revision 2 (USEPA, 1992). Ion exchange and mass spectrometry procedures are similar to those reported by Tatsumoto and Unruh (1976) and Fey and others (1999) with minor modifications to accommodate a larger sample size and the metal-rich nature of the samples. A detailed description of the chemical procedures may be found in Appendix 1.

Samples were loaded onto single rhenium filaments using the conventional silica gel-phosphoric acid technique (e.g. Tatsumoto and Unruh, 1976). Mass spectrometry was performed using a VG Sector-54, 7-collector, solid source, thermal-ionization mass spectrometer operated in "static" mode. Data were acquired with the "Sector 54, version 3.974" software package provided by the manufacturer of the mass spectrometer. All samples and standards were run using collectors L1, H1, H2, and H3 for ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively.

Quality Assurance and Quality Control (QA and QC)

Samples were initially submitted by USEPA to the analyst without context. Although Pb contents were provided so that the appropriate amount of sample could be processed, the nature of the sample (soil, herbicide, smelter waste, etc.) and the arsenic contents in the samples remained unknown to the analyst until after the first draft of this report was completed. Additional information was then provided so that this report could be completed in a comprehensive manner.

After the first draft of this report was submitted to USEPA for review, fourteen additional residential soils were selected for analyses. Samples were received by the analyst in April and May of 2001. These samples were selected jointly by USEPA and USGS personnel to encompass the complete ranges of lead and arsenic contents within the soils. Included within these additional soils were five samples from a single residential property. These were selected in order to test the validity of simple mixing models.

Quality Assurance and control procedures and results are provided in Appendix 2. The principal source of analytical uncertainty in lead isotopic analyses is from correction for mass fractionation induced during mass spectrometry. Mass fractionation was monitored using NIST

standard SRM-981 (Cantanzaro and others, 1968; Todt and others, 1993). A second NIST standard, SRM-982 (Cantanzaro and others, 1968; Todt and others, 1993) was measured as a check of the correction procedures (Appendix 2).

Two Pb blanks were determined during the course of this study, one for the acid and hydrogen peroxide digestion procedure alone and one for total chemistry of a 1 ml aliquot from the acid digestion (Appendix 2). The Pb blank for the acid digestion was 0.3 ng (10^{-9} g) and that for the total chemistry was 0.09 ng. These values correspond to less than 0.004% and 0.02% of the lead in the total samples and solution aliquots, respectively. Consequently, no blank correction was applied to the isotopic data (see Appendix 2).

Three types of replicate samples were analyzed; (1) Blind duplicates submitted by USEPA, (2) Replicate acid-hydrogen peroxide digestions of the same (digestion replicates), and (3) Replicate loads of the same sample from a single chemical procedure (mass spectrometry replicates). Results for the replicate analyses are presented in Table 2, and Appendix 2 (Tables A2-3, and A2-4).

Chain of Custody (COC)

Samples were handled in accordance with U.S. Geological Survey chain-of-custody procedures (Murphy and others, 1997). Samples were received from the USGS sample control custodian in a sealed box by the analyst and were hand-carried to the laboratory where they remained for the duration of the study. The laboratory is secured with a combination lock with a combination known only to the analyst. Individual samples were enclosed in bags sealed and dated by USEPA. The analyst found all seals to be intact upon receipt.

The mass spectrometer used to acquire data was secured with two padlocks to lock the sample access door. The computer that was used to reduce the data was also secured with a lock supplied by the manufacturer that prevented access to the keyboard. Both the mass spectrometer and computer were kept locked at all times during the study and all keys were retained exclusively by the analyst.

Analytical Results and Discussion

Lead Isotopic Compositions

A total of thirty-four selected samples were analyzed for lead isotopic compositions. These included twenty-six residential soils (plus two blind duplicates), one procedural blank, two soils from a local smelter, and one sample of smelter waste from the same smelter. Also analyzed were a sample of "PAX", an arsenic trioxide plus lead arsenate herbicide that was

commercially available during the 1950's through the early 1970's, and a sample of Acme brand lead arsenate pesticide that was also commercially available during this time frame.

Sample numbers and sample types as well as lead and arsenic concentrations for the samples are summarized in Table 1 (USEPA, written communication, 2000, 2001). Residential soil samples are listed high-As, intermediate-As or low-As and as either "focal" or "adjacent". Focal samples are those that were collected from a specific property, whereas adjacent samples were collected from property adjacent the specific property. Adjacent samples all show relatively low As levels (Table 1).

Lead isotopic data for the samples are shown in Table 2. Each entry represents a separate mass spectrometer run. Entries with identical sample numbers are mass spectrometry replicates measured from a single processed aliquot of sample. Entries with the same sample number but different suffix letters (e.g. 642B-A, 642B-B, 642B-C) are digestion replicates obtained from separate acid and hydrogen peroxide digestions of the sample.

Both the raw data and data corrected for mass fractionation are shown. The precision for the raw data is given as the percent standard error (1 S.E. = 1 sigma-mean) calculated by the on line data-acquisition software. Analytical uncertainties for the corrected data are shown as absolute values and are calculated at the 95% confidence interval (C.I., Ludwig, 1994). Weighted mean values, also calculated at the 95% C.I., are shown for the mass spectrometry replicates and, where appropriate, grand mean values are calculated for each sample from the means of the digestion replicates. The mean values for the individual samples are shown in bold type in Table 2.

The lead isotopic data are summarized on conventional $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams in Figure 1. Each data point represents the mean value for an individual sample (Table 2) and data are coded according to their Pb contents (Table 1). The data yield moderately well correlated linear arrays with $r^2 = 0.854$ and 0.812 for the $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams, respectively (unweighted; r^2 is defined by the plotting software, Deltagraph 4.0, as the square of the regression correlation coefficient). Also shown by error ellipses in Figure 1 are typical analytical uncertainties for a single mass spectrometer run ($\pm 0.09\%$ for $^{206}Pb/^{204}Pb$, $\pm0.13\%$ for $^{207}Pb/^{204}Pb$, and $\pm0.18\%$ for $^{208}Pb/^{204}Pb$).

Samples with the lowest Pb contents are characterized by radiogenic Pb ($^{206}Pb/^{204}Pb >$ 18.4) and slightly elevated $^{208}Pb/^{204}Pb$ relative to the other samples. Residential soils with the highest Pb contents form two distinct clusters; one with $^{206}Pb/^{204}Pb > 18.5$ and one with $^{206}Pb/^{204}Pb < 18.0$. The data from the remaining residential soils plot between the extremes defined by the low-Pb and two high-Pb groups.

Table 1. Sample numbers, sample types, and lead and arsenic concentrations in selected samples from the VBI70 study.

Sample Number	EPA Code No.	Sample type	Location[1]	As ppm[2]	Pb ppm[3]
3-15639-B	3-15669-R	Acme brand Lead Arsenate		273000	128000
3-15641-B	SC-00006	High-As residential soil	Focal	836	1490
3-15642-B	SC-00010	Intermediate As residential	Focal	173	422
3-15643-B	SC-00011	Smelter Site soil		22400	4520
3-15644-B	SC-00017	Low As residential soil	Adjacent	9	39
3-15645-B	SC-00018	Smelter Site soil		27200	5660
3-15646-B	SC-00023	Smelter material		7630	2160
3-15647-B	SC-00025	Low As residential soil	Focal	24	126
3-15648-B	SC-00027	Intermediate As residential	Focal	165	115
3-15649-B	SC-00039	Low As residential soil	Focal	25	92
3-15650-B	SC-00046	High-As residential soil	Focal	1490	1560
3-15651-B	SC-00046	Duplicate		1490	1560
3-15652-B	SC-00048	High-As residential soil	Adjacent	35	261
3-15653-B	SC-00065	Baseline soil	Focal	7	101
3-15654-B	SC-00065	Duplicate		7	101
3-15655-B	SC-00069	High-As residential soil	Adjacent	15	151
3-15656-B	SC-00084	Intermediate As residential	Adjacent	23	175
3-15657-B	SC-00104	High-As residential soil	Focal	1490	1140
3-15658-B	SC-00099	PAX		120000	24300
3-15659-B		Prep. Blank		n.d.	n.d.
Samples received 4/01-5/01					
3-13569-B		High-As residential soil	Focal	1492	409
3-13989-B		High-As residential soil	Focal	904	302
3-02246-B		Low As residential soil	Focal	<11	1658
3-10319-B		Low As residential soil	Focal	48	1469
3-12524-B	-	High-As residential soil	Focal	1135	794
3-12820-B		Intermediate As residential	Focal	242	607
3-01182-B		Low As residential soil	Focal	14	720
3-00748-B		Intermediate As residential	Focal	409	633
3-10740-B		Low As residential soil	Focal	23	984
Samples from a single residential property					
3-12152-B		Low As residential soil	Focal	<11	1730
3-12040-B		Low As residential soil	Focal	<11	256
3-12039-B		Low As residential soil	Focal	15	413
3-12035-B		Low As residential soil	Focal	26	824
3-12151-B		Intermediate As residential	Focal	221	540

[1]Focal samples are those collected at the site indicted by the sample type. Adjacent samples are those collected adjacent to the indicated sample type.

[2] As concentrations provided by USEPA (written communication, 2001).

[3] Pb concentrations provided by USEPA (written communication, 2000; 2001).

Table 2. Lead Isotopic compositions in acid digestions of selected soils samples from the Vasquez Blvd.-I70 Project.

Lab No/EPA No.[3]	Pb ppm[4]	Type	$^{206}Pb/^{204}Pb$	% S.E.	$^{207}Pb/^{206}Pb$	% S.E.	$^{208}Pb/^{206}Pb$	% S.E.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
					Raw Data[1]						Corrected for mass fractionation[2]		
3-15639-B		Pb Arsenate											
3-15660-B													
639B			18.0453	0.0016	0.860891	0.0007	2.10038	0.0010	18.075 ± 0.016	0.86158 ± 0.00037	2.1037 ± 0.0018	15.573 ± 0.021	38.024 ± 0.067
639B			18.0497	0.0027	0.860973	0.0010	2.10094	0.0016	18.079 ± 0.016	0.86166 ± 0.00037	2.1042 ± 0.0018	15.578 ± 0.021	38.043 ± 0.067
639B			18.0303	0.0020	0.860519	0.0008	2.09888	0.0016	18.060 ± 0.016	0.86120 ± 0.00037	2.1021 ± 0.0018	15.553 ± 0.021	37.985 ± 0.067
Mean	128000								18.071 ± 0.009	0.86148 ± 0.00044	2.1033 ± 0.0010	15.568 ± 0.023	38.009 ± 0.038
3-15641-B		Res. Soil											
SC-00006													
641B			17.8760	0.0030	0.867917	0.0007	2.10752	0.0009	17.906 ± 0.016	0.86861 ± 0.00037	2.1108 ± 0.0018	15.553 ± 0.021	37.795 ± 0.067
641B			17.8998	0.0072	0.868387	0.0031	2.10999	0.0064	17.929 ± 0.017	0.86906 ± 0.00038	2.1133 ± 0.0019	15.582 ± 0.021	37.890 ± 0.067
641B			17.8656	0.0033	0.867646	0.0008	2.10613	0.0006	17.895 ± 0.016	0.86834 ± 0.00037	2.1094 ± 0.0018	15.539 ± 0.021	37.746 ± 0.067
Mean	1490								17.910 ± 0.039	0.86867 ± 0.00083	2.1112 ± 0.0046	15.558 ± 0.050	37.812 ± 0.163
3-15642-B		Res. Soil											
SC-00010													
642B-A			18.2064	0.0031	0.854041	0.0014	2.09149	0.0024	18.236 ± 0.017	0.85472 ± 0.00037	2.0947 ± 0.0018	15.587 ± 0.021	38.201 ± 0.067
642B-A			18.2260	0.0064	0.854359	0.0023	2.09344	0.0053	18.256 ± 0.017	0.85504 ± 0.00037	2.0967 ± 0.0018	15.610 ± 0.021	38.278 ± 0.067
642B-A			18.2150	0.0093	0.854019	0.0025	2.09192	0.0045	18.245 ± 0.017	0.85470 ± 0.00037	2.0952 ± 0.0018	15.594 ± 0.021	38.227 ± 0.067
642B-A			18.2198	0.0063	0.853997	0.0025	2.09185	0.0054	18.250 ± 0.017	0.85468 ± 0.00037	2.0951 ± 0.0018	15.598 ± 0.021	38.235 ± 0.067
642B-A			18.2284	0.0127	0.853709	0.0026	2.09137	0.0044	18.258 ± 0.018	0.85439 ± 0.00038	2.0946 ± 0.0018	15.600 ± 0.021	38.245 ± 0.067
Mean									18.249 ± 0.007	0.85471 ± 0.00021	2.0953 ± 0.0008	15.598 ± 0.009	38.237 ± 0.029
642B-B			18.1881	0.0041	0.854971	0.0013	2.09284	0.0015	18.218 ± 0.017	0.85565 ± 0.00037	2.0961 ± 0.0018	15.588 ± 0.021	38.187 ± 0.067
642B-B			18.2038	0.0043	0.855349	0.0020	2.09467	0.0043	18.234 ± 0.017	0.85603 ± 0.00037	2.0979 ± 0.0018	15.609 ± 0.021	38.253 ± 0.067
642B-B			18.1755	0.0023	0.854746	0.0010	2.09143	0.0017	18.205 ± 0.016	0.85543 ± 0.00037	2.0947 ± 0.0018	15.573 ± 0.021	38.135 ± 0.067
Mean									18.219 ± 0.031	0.85570 ± 0.00065	2.0962 ± 0.0036	15.590 ± 0.039	38.191 ± 0.128
642B-C			18.2174	0.0016	0.854590	0.0005	2.09349	0.0006	18.247 ± 0.016	0.85527 ± 0.00037	2.0968 ± 0.0018	15.607 ± 0.021	38.260 ± 0.067
642B-C			18.2150	0.0021	0.854463	0.0009	2.09260	0.0018	18.245 ± 0.017	0.85514 ± 0.00037	2.0961 ± 0.0018	15.602 ± 0.021	38.243 ± 0.067
642B-C			18.2080	0.0015	0.854244	0.0006	2.09199	0.0009	18.238 ± 0.016	0.85492 ± 0.00037	2.0952 ± 0.0018	15.592 ± 0.021	38.213 ± 0.067
Mean									18.243 ± 0.009	0.85511 ± 0.00021	2.0960 ± 0.0010	15.600 ± 0.012	38.237 ± 0.038
Mean 642B A-C	422								18.242 ± 0.029	0.85509 ± 0.00094	2.0956 ± 0.0006	15.599 ± 0.007	38.235 ± 0.023
3-15643-B		Smelter Soil											
SC-00011													
643B			18.1681	0.0023	0.855456	0.0010	2.09202	0.0020	18.196 ± 0.016	0.85614 ± 0.00037	2.0953 ± 0.0018	15.578 ± 0.021	38.126 ± 0.067
643B			18.1539	0.0037	0.855205	0.0011	2.09088	0.0019	18.184 ± 0.017	0.85589 ± 0.00037	2.0939 ± 0.0018	15.563 ± 0.021	38.076 ± 0.067
Mean	4520								18.190 ± 0.011	0.85601 ± 0.00026	2.0946 ± 0.0013	15.570 ± 0.014	38.101 ± 0.046
3-15644-B		Res. Soil											
SC-00017													
644B-A			18.4188	0.0026	0.844483	0.0011	2.09277	0.0014	18.449 ± 0.017	0.84516 ± 0.00037	2.0960 ± 0.0018	15.592 ± 0.021	38.670 ± 0.068
644B-A			18.4243	0.0037	0.844582	0.0012	2.09333	0.0027	18.455 ± 0.017	0.84525 ± 0.00037	2.0966 ± 0.0018	15.599 ± 0.021	38.692 ± 0.068
Mean									18.452 ± 0.012	0.84521 ± 0.00025	2.0963 ± 0.0013	15.595 ± 0.014	38.681 ± 0.046
644B-B			18.4670	0.0026	0.841463	0.0010	2.09140	0.0021	18.497 ± 0.017	0.84213 ± 0.00036	2.0947 ± 0.0018	15.577 ± 0.021	38.746 ± 0.068
644B-C			18.5792	0.0062	0.839810	0.0025	2.10998	0.0052	18.610 ± 0.017	0.84048 ± 0.00037	2.1133 ± 0.0019	15.641 ± 0.021	39.328 ± 0.069
Mean 644B A-C	39								18.52 ± 0.20	0.8426 ± 0.0061	2.101 ± 0.023	15.604 ± 0.080	38.92 ± 0.90

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Table 2. Contd.

Lab No/EPA No.[?]	Pb ppm[1]	Type	Raw Data[1]						Corrected for mass fractionation[1]				
			$^{206}Pb/^{204}Pb$	% S.E.	$^{207}Pb/^{204}Pb$	% S.E.	$^{208}Pb/^{204}Pb$	% S.E.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
3-15645-B		Smelter Soil											
SC-00018													
645B			18.0919	0.0022	0.857832	0.0007	2.09510	0.0009	18.122 ± 0.016	0.85852 ± 0.00037	2.0984 ± 0.0018	15.556 ± 0.021	38.026 ± 0.067
645B			18.0911	0.0027	0.857847	0.0007	2.09515	0.0009	18.121 ± 0.016	0.85853 ± 0.00037	2.0984 ± 0.0018	15.557 ± 0.021	38.025 ± 0.067
Mean	5660								18.122 ± 0.011	0.85852 ± 0.00026	2.0984 ± 0.0013	15.557 ± 0.014	38.026 ± 0.046
3-15646-B		Smelter											
SC-00023		Material											
646B			18.0984	0.0022	0.857802	0.0007	2.09641	0.0015	18.128 ± 0.016	0.85849 ± 0.00037	2.0997 ± 0.0018	15.563 ± 0.021	38.063 ± 0.067
646B			18.0898	0.0041	0.857609	0.0009	2.09536	0.0016	18.120 ± 0.017	0.85829 ± 0.00037	2.0986 ± 0.0018	15.552 ± 0.021	38.026 ± 0.067
646B			18.0876	0.0058	0.857621	0.0011	2.09541	0.0012	18.117 ± 0.017	0.85830 ± 0.00037	2.0987 ± 0.0018	15.550 ± 0.021	38.023 ± 0.067
Mean	2160								18.122 ± 0.009	0.85836 ± 0.00021	2.0990 ± 0.0010	15.555 ± 0.012	38.037 ± 0.038
3-15647-B		Res. Soil											
SC-00025													
647B			18.4147	0.0019	0.845385	0.0007	2.08550	0.0011	18.445 ± 0.017	0.84606 ± 0.00036	2.0887 ± 0.0018	15.606 ± 0.021	38.527 ± 0.068
647B			18.4188	0.0034	0.845532	0.0011	2.08635	0.0012	18.449 ± 0.017	0.84621 ± 0.00037	2.0896 ± 0.0018	15.612 ± 0.021	38.551 ± 0.068
Mean	126								18.447 ± 0.012	0.84613 ± 0.00025	2.0891 ± 0.0013	15.609 ± 0.014	38.539 ± 0.046
3-15648-B		Res. Soil											
SC-00027													
648B	115		18.3796	0.0125	0.846401	0.0031	2.08402	0.0059	18.410 ± 0.016	0.84706 ± 0.00037	2.0873 ± 0.0018	15.595 ± 0.021	38.426 ± 0.068
3-15649-B		Res. Soil											
SC-00039													
649B			18.3848	0.0017	0.848386	0.0006	2.09495	0.0010	18.395 ± 0.017	0.84906 ± 0.00037	2.0982 ± 0.0018	15.610 ± 0.021	38.597 ± 0.068
649B			18.3445	0.0034	0.847974	0.0013	2.09255	0.0029	18.375 ± 0.017	0.84865 ± 0.00037	2.0956 ± 0.0018	15.594 ± 0.021	38.510 ± 0.068
649B			18.3865	0.0038	0.848447	0.0010	2.09514	0.0010	18.397 ± 0.017	0.84912 ± 0.00037	2.0984 ± 0.0018	15.621 ± 0.021	38.604 ± 0.068
Mean	92								18.389 ± 0.024	0.84894 ± 0.00049	2.0975 ± 0.0031	15.611 ± 0.030	38.570 ± 0.108
3-15650-B		Res. Soil											
SC-00046													
650B			17.7702	0.0018	0.873614	0.0006	2.11319	0.0007	17.800 ± 0.016	0.87431 ± 0.00038	2.1165 ± 0.0018	15.562 ± 0.021	37.672 ± 0.066
650B			17.7698	0.0030	0.873548	0.0009	2.11310	0.0013	17.799 ± 0.016	0.87424 ± 0.00038	2.1164 ± 0.0018	15.561 ± 0.021	37.670 ± 0.066
650B			17.7741	0.0032	0.873617	0.0012	2.11347	0.0023	17.803 ± 0.016	0.87431 ± 0.00038	2.1168 ± 0.0018	15.566 ± 0.021	37.686 ± 0.066
Mean	1560								17.801 ± 0.009	0.87429 ± 0.00021	2.1166 ± 0.0010	15.563 ± 0.012	37.676 ± 0.038
3-15651-B		Res. Soil											
SC-00046 DUP													
651B			17.7556	0.0025	0.874082	0.0012	2.11399	0.0013	17.785 ± 0.016	0.87478 ± 0.00038	2.1173 ± 0.0018	15.558 ± 0.021	37.656 ± 0.066
651B			17.7692	0.0070	0.874419	0.0024	2.11596	0.0055	17.799 ± 0.017	0.87512 ± 0.00038	2.1193 ± 0.0019	15.576 ± 0.021	37.720 ± 0.066
651B			17.7534	0.0038	0.873984	0.0011	2.11349	0.0018	17.783 ± 0.016	0.87468 ± 0.00038	2.1168 ± 0.0018	15.554 ± 0.021	37.642 ± 0.066
Mean	1560								17.789 ± 0.009	0.87486 ± 0.00022	2.1178 ± 0.0025	15.563 ± 0.012	36.673 ± 0.037
3-15652-B		Res. Soil											
SC-00048													
652B			18.3237	0.0018	0.849612	0.0007	2.08176	0.0010	18.354 ± 0.017	0.85029 ± 0.00037	2.0850 ± 0.0018	15.608 ± 0.021	38.268 ± 0.067
652B			18.3164	0.0024	0.849428	0.0010	2.08098	0.0021	18.347 ± 0.017	0.85010 ± 0.00037	2.0842 ± 0.0018	15.597 ± 0.021	38.238 ± 0.067
Mean	261								18.351 ± 0.012	0.85019 ± 0.00026	2.0846 ± 0.0013	15.601 ± 0.014	38.253 ± 0.046

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Table 2. Contd.

Lab No/EPA No.[3]	Pb ppm[4]	Type	Raw Data[1]						Corrected for mass fractionation[3]				
			²⁰⁶Pb/²⁰⁴Pb	% S.E.	²⁰⁷Pb/²⁰⁶Pb	% S.E.	²⁰⁸Pb/²⁰⁶Pb	% S.E.	²⁰⁶Pb/²⁰⁴Pb	²⁰⁷Pb/²⁰⁶Pb	²⁰⁸Pb/²⁰⁶Pb	²⁰⁷Pb/²⁰⁴Pb	²⁰⁸Pb/²⁰⁴Pb
3-15653-B SC-00065		Baseline Soil											
653B			18.3800	0.0024	0.846355	0.0007	2.08585	0.0009	18.410 ± 0.017	0.84703 ± 0.00037	2.0891 ± 0.0018	15.594 ± 0.021	38.461 ± 0.068
653B			18.3816	0.0032	0.846356	0.0010	2.08571	0.0019	18.412 ± 0.017	0.84703 ± 0.00037	2.0890 ± 0.0018	15.595 ± 0.021	38.462 ± 0.068
653B			18.3860	0.0030	0.846417	0.0012	2.08631	0.0026	18.416 ± 0.017	0.84709 ± 0.00037	2.0896 ± 0.0018	15.600 ± 0.021	38.482 ± 0.068
Mean	101								18.413 ± 0.009	0.84705 ± 0.00020	2.0892 ± 0.0010	15.596 ± 0.012	38.468 ± 0.038
3-15654-B SC-00065 DUP		Baseline Soil											
654B-A			18.8272	0.0048	0.827089	0.0022	2.04636	0.0049	18.858 ± 0.017	0.82775 ± 0.00036	2.0496 ± 0.0018	15.610 ± 0.021	38.651 ± 0.068
654B-A			18.8487	0.0029	0.827383	0.0008	2.04795	0.0014	18.878 ± 0.017	0.82804 ± 0.00036	2.0511 ± 0.0018	15.632 ± 0.021	38.721 ± 0.068
654B-A			18.8414	0.0026	0.827372	0.0013	2.04786	0.0025	18.872 ± 0.017	0.82803 ± 0.00036	2.0511 ± 0.0018	15.627 ± 0.021	38.708 ± 0.068
Mean									18.869 ± 0.010	0.82794 ± 0.00021	2.0506 ± 0.0010	15.623 ± 0.012	38.693 ± 0.039
654B-B			18.4285	0.0045	0.844454	0.0012	2.08549	0.0018	18.459 ± 0.017	0.84513 ± 0.00037	2.0887 ± 0.0018	15.600 ± 0.021	38.556 ± 0.068
654B-C			18.4232	0.0075	0.845692	0.0014	2.08653	0.0012	18.454 ± 0.017	0.84637 ± 0.00037	2.0898 ± 0.0018	15.619 ± 0.021	38.564 ± 0.068
654B-D			18.4659	0.0029	0.843491	0.0011	2.08544	0.0018	18.496 ± 0.017	0.84416 ± 0.00036	2.0887 ± 0.0018	15.614 ± 0.021	38.633 ± 0.068
654B-E			18.3547	0.0023	0.847687	0.0008	2.08618	0.0016	18.385 ± 0.017	0.84836 ± 0.00037	2.0894 ± 0.0018	15.597 ± 0.021	38.414 ± 0.068
654B-F			18.4291	0.0016	0.844134	0.0008	2.08531	0.0015	18.460 ± 0.017	0.84481 ± 0.00036	2.0886 ± 0.0018	15.595 ± 0.021	38.554 ± 0.068
Mean 654B B-F	101								18.451 ± 0.050	0.8456 ± 0.0020	2.0890 ± 0.0008	15.605 ± 0.009	38.544 ± 0.096
3-15655-B SC-00069		Res. Soil											
655B-A			18.2694	0.0018	0.851860	0.0007	2.08647	0.0014	18.300 ± 0.017	0.85256 ± 0.00037	2.0897 ± 0.0018	15.601 ± 0.021	38.241 ± 0.067
655B-A			18.2648	0.0017	0.851734	0.0004	2.08594	0.0010	18.295 ± 0.017	0.85241 ± 0.00037	2.0892 ± 0.0018	15.595 ± 0.021	38.222 ± 0.067
Mean									18.297 ± 0.011	0.85249 ± 0.00026	2.0894 ± 0.0013	15.598 ± 0.014	38.231 ± 0.046
655B-B			18.2823	0.0025	0.850617	0.0006	2.08327	0.0015	18.312 ± 0.017	0.85129 ± 0.00037	2.0865 ± 0.0018	15.589 ± 0.021	38.209 ± 0.067
Mean 655B A-B	151								18.303 ± 0.073	0.8519 ± 0.0073	2.088 ± 0.017	15.595 ± 0.011	38.224 ± 0.037
3-15656-B SC-00084		Res. Soil											
656B-A			18.4515	0.0035	0.844073	0.0017	2.06797	0.0035	18.482 ± 0.017	0.84475 ± 0.00037	2.0712 ± 0.0018	15.613 ± 0.021	38.280 ± 0.067
656B-A			18.4479	0.0024	0.844073	0.0008	2.06751	0.0018	18.478 ± 0.017	0.84475 ± 0.00036	2.0707 ± 0.0018	15.609 ± 0.021	38.264 ± 0.067
656B-A			18.4502	0.0032	0.844119	0.0011	2.06803	0.0011	18.481 ± 0.017	0.84479 ± 0.00036	2.0713 ± 0.0018	15.612 ± 0.021	38.278 ± 0.067
Mean									18.480 ± 0.010	0.84476 ± 0.00020	2.0711 ± 0.0010	15.611 ± 0.012	38.274 ± 0.038
656B-B			17.9549	0.0021	0.864978	0.0006	2.09423	0.0015	17.985 ± 0.016	0.86567 ± 0.00037	2.0975 ± 0.0018	15.569 ± 0.021	37.722 ± 0.067
656B-C			18.5411	0.0042	0.840091	0.0019	2.06893	0.0041	18.572 ± 0.017	0.84076 ± 0.00037	2.0722 ± 0.0018	15.614 ± 0.021	38.483 ± 0.068
656B-D			18.3719	0.0029	0.846875	0.0013	2.06935	0.0027	18.402 ± 0.017	0.84755 ± 0.00037	2.0726 ± 0.0018	15.597 ± 0.021	38.140 ± 0.067
656B-E			18.3958	0.0036	0.845958	0.0014	2.06725	0.0028	18.426 ± 0.017	0.84663 ± 0.00037	2.0705 ± 0.0018	15.600 ± 0.021	38.151 ± 0.067
Mean 656B A, C-E	175								18.47 ± 0.12	0.8449 ± 0.0042	2.0714 ± 0.0007	15.607 ± 0.008	38.26 ± 0.25

Table 2. Contd.

Lab No/EPA No.[3]	Pb ppm[4]	Type	Raw Data[1]						Corrected for mass fractionation[1]				
			$^{206}Pb/^{204}Pb$	% S.E.	$^{207}Pb/^{206}Pb$	% S.E.	$^{208}Pb/^{206}Pb$	% S.E.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
3-15657-B		Res. Soil											
SC-00104													
657B-A			17.8771	0.0020	0.868880	0.0007	2.10983	0.0010	17.907 ± 0.016	0.86957 ± 0.00037	2.1131 ± 0.0018	15.571 ± 0.021	37.839 ± 0.067
657B-A			17.8647	0.0017	0.868628	0.0006	2.10861	0.0017	17.894 ± 0.016	0.86932 ± 0.00037	2.1119 ± 0.0018	15.556 ± 0.021	37.791 ± 0.067
Mean									17.900 ± 0.011	0.86944 ± 0.00026	2.1125 ± 0.0013	15.563 ± 0.014	37.815 ± 0.045
657B-B			17.8650	0.0020	0.869417	0.0006	2.11025	0.0009	17.894 ± 0.016	0.87011 ± 0.00037	2.1135 ± 0.0018	15.570 ± 0.021	37.821 ± 0.067
Mean 657B A-B	1140								17.898 ± 0.009	0.8698 ± 0.0040	2.1128 ± 0.0010	15.565 ± 0.011	37.817 ± 0.037
3-15658-B		PAX											
SC-00099													
858B			17.1742	0.0046	0.900857	0.0019	2.14007	0.0042	17.203 ± 0.016	0.90157 ± 0.00039	2.1434 ± 0.0019	15.509 ± 0.021	36.872 ± 0.065
858B			17.1802	0.0045	0.900985	0.0012	2.14095	0.0029	17.209 ± 0.016	0.90168 ± 0.00039	2.1443 ± 0.0019	15.517 ± 0.021	36.900 ± 0.065
Mean	24300								17.206 ± 0.011	0.90162 ± 0.00027	2.1438 ± 0.0013	15.513 ± 0.014	36.886 ± 0.044
3-15659-B		prep. blank											
n.a.													
659B			18.0854	0.0036	0.859095	0.0013	2.10784	0.0029	18.115 ± 0.016	0.85978 ± 0.00037	2.1111 ± 0.0018	15.575 ± 0.021	38.244 ± 0.067
659B			18.0961	0.0035	0.859319	0.0010	2.10869	0.0020	18.126 ± 0.016	0.86000 ± 0.00037	2.1120 ± 0.0018	15.588 ± 0.021	38.282 ± 0.067
Mean	n.d.								18.120 ± 0.011	0.85989 ± 0.00026	2.1116 ± 0.0013	15.581 ± 0.014	38.263 ± 0.046
Samples Received 4/01-5/01													
3-13569-B		Res. Soil											
569B			17.9083	0.0032	0.867088	0.0015	2.10132	0.0028	17.937 ± 0.012	0.86773 ± 0.00038	2.1047 ± 0.0015	15.565 ± 0.017	37.753 ± 0.051
569B			17.8966	0.0031	0.866801	0.0013	2.09988	0.0027	17.925 ± 0.012	0.86747 ± 0.00038	2.1031 ± 0.0015	15.550 ± 0.017	37.699 ± 0.051
569B			17.8991	0.0024	0.866658	0.0011	2.09903	0.0115	17.928 ± 0.011	0.86732 ± 0.00037	2.1025 ± 0.0017	15.549 ± 0.017	37.692 ± 0.051
Mean	409								17.930 ± 0.006	0.86751 ± 0.00021	2.1035 ± 0.0023	15.555 ± 0.010	37.715 ± 0.060
3-13989-B		Res. Soil											
989B			18.1118	0.0027	0.857606	0.0009	2.08895	0.0018	18.141 ± 0.012	0.85826 ± 0.00037	2.0924 ± 0.0015	15.570 ± 0.017	37.957 ± 0.051
989B			18.1274	0.0038	0.857861	0.0014	2.09051	0.0030	18.156 ± 0.012	0.85854 ± 0.00037	2.0939 ± 0.0015	15.588 ± 0.017	38.016 ± 0.051
989B			18.1228	0.0024	0.857770	0.0010	2.08976	0.0019	18.152 ± 0.012	0.85843 ± 0.00037	2.0932 ± 0.0015	15.582 ± 0.017	37.994 ± 0.051
Mean	302								18.150 ± 0.014	0.85841 ± 0.00021	2.0932 ± 0.0009	15.580 ± 0.010	37.990 ± 0.029
3-12524-B		Res. Soil											
524B			18.1449	0.0025	0.856547	0.0008	2.08839	0.0019	18.174 ± 0.012	0.85720 ± 0.00037	2.0918 ± 0.0015	15.579 ± 0.017	38.016 ± 0.051
524B			18.1597	0.0026	0.856876	0.0007	2.09052	0.0011	18.189 ± 0.012	0.85753 ± 0.00037	2.0939 ± 0.0015	15.598 ± 0.018	38.086 ± 0.052
524B			18.1518	0.0022	0.856461	0.0005	2.08830	0.0005	18.181 ± 0.012	0.85712 ± 0.00037	2.0917 ± 0.0015	15.583 ± 0.017	38.029 ± 0.051
Mean	794								18.181 ± 0.013	0.85728 ± 0.00021	2.0925 ± 0.0027	15.587 ± 0.010	38.044 ± 0.072
3-12820-B		Res. Soil											
820B			17.9056	0.0038	0.866940	0.0016	2.10109	0.0031	17.934 ± 0.012	0.86761 ± 0.00038	2.1045 ± 0.0015	15.560 ± 0.017	37.743 ± 0.051
820B			17.8936	0.0036	0.866585	0.0014	2.09940	0.0024	17.922 ± 0.012	0.86725 ± 0.00038	2.1028 ± 0.0015	15.543 ± 0.017	37.687 ± 0.051
820B			17.9225	0.0039	0.867176	0.0014	2.10287	0.0027	17.951 ± 0.012	0.86784 ± 0.00038	2.1063 ± 0.0015	15.579 ± 0.017	37.811 ± 0.051
Mean	607								17.936 ± 0.034	0.86757 ± 0.00063	2.1045 ± 0.0042	15.561 ± 0.040	37.750 ± 0.143
3-01182-B		Res. Soil											
182B			18.3017	0.0028	0.849789	0.0013	2.07692	0.0023	18.331 ± 0.012	0.85044 ± 0.00037	2.0803 ± 0.0015	15.589 ± 0.017	38.134 ± 0.052
182B			18.3136	0.0035	0.849914	0.0010	2.07790	0.0020	18.343 ± 0.012	0.85057 ± 0.00037	2.0813 ± 0.0015	15.602 ± 0.018	38.177 ± 0.052
182B			18.3204	0.0018	0.850153	0.0005	2.07809	0.0007	18.350 ± 0.012	0.85081 ± 0.00037	2.0815 ± 0.0015	15.612 ± 0.018	38.195 ± 0.052
Mean	720								18.341 ± 0.020	0.85061 ± 0.00020	2.0810 ± 0.0009	15.601 ± 0.022	38.169 ± 0.029

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Table 2. Contd.

Lab No/EPA No.[?]	Pb ppm[4]	Type	Raw Data[1] 206Pb/204Pb	% S.E.	207Pb/206Pb	% S.E.	208Pb/206Pb	% S.E.	Corrected for mass fractionation[3] 206Pb/204Pb	207Pb/206Pb	208Pb/206Pb	207Pb/204Pb	208Pb/204Pb
3-00748-B		Res. Soil											
748B			18.2789	0.0028	0.850419	0.0010	2.07145	0.0019	18.308 ± 0.012	0.85107 ± 0.00037	2.0748 ± 0.0015	15.582 ± 0.017	37.986 ± 0.051
748B			18.2874	0.0038	0.850664	0.0015	2.07265	0.0029	18.317 ± 0.012	0.85132 ± 0.00037	2.0760 ± 0.0015	15.593 ± 0.018	38.026 ± 0.051
748B			18.2928	0.0031	0.850621	0.0008	2.07259	0.0016	18.322 ± 0.012	0.85127 ± 0.00037	2.0760 ± 0.0015	15.597 ± 0.018	38.036 ± 0.051
Mean	633								18.316 ± 0.007	0.85122 ± 0.00020	2.0756 ± 0.0009	15.591 ± 0.010	38.016 ± 0.029
3-10740-B		Res. Soil											
740B			18.3013	0.0046	0.848982	0.0022	2.07074	0.0041	18.331 ± 0.012	0.84963 ± 0.00037	2.0741 ± 0.0015	15.574 ± 0.017	38.020 ± 0.051
740B			18.3032	0.0057	0.849057	0.0014	2.07117	0.0013	18.333 ± 0.012	0.84971 ± 0.00037	2.0745 ± 0.0015	15.577 ± 0.017	38.032 ± 0.051
Mean	984								18.332 ± 0.008	0.84967 ± 0.00025	2.0743 ± 0.0010	15.575 ± 0.012	38.026 ± 0.036
3-02246-B		Res. Soil											
246B			18.5659	0.0041	0.840295	0.0011	2.06094	0.0026	18.596 ± 0.012	0.84094 ± 0.00036	2.0643 ± 0.0015	15.638 ± 0.018	38.387 ± 0.052
246B			18.5591	0.0025	0.840132	0.0007	2.05935	0.0009	18.589 ± 0.012	0.84078 ± 0.00036	2.0627 ± 0.0015	15.629 ± 0.018	38.343 ± 0.052
Mean	1658								18.593 ± 0.008	0.84086 ± 0.00025	2.0635 ± 0.0056	15.633 ± 0.012	38.365 ± 0.036
3-10319-B		Res. Soil											
319B			18.8051	0.0033	0.829795	0.0014	2.04272	0.0029	18.835 ± 0.012	0.83043 ± 0.00036	2.0461 ± 0.0015	15.641 ± 0.018	38.538 ± 0.052
319B			18.8080	0.0029	0.829640	0.0010	2.04198	0.0016	18.838 ± 0.012	0.83028 ± 0.00036	2.0453 ± 0.0015	15.641 ± 0.018	38.530 ± 0.052
Mean	1469								18.837 ± 0.008	0.83035 ± 0.00025	2.0457 ± 0.0010	15.641 ± 0.012	38.534 ± 0.036
Samples from a single residential property													
3-12152-B		Res. Soil											
152B-A			17.5876	0.0025	0.880346	0.0013	2.11644	0.0026	17.616 ± 0.011	0.88102 ± 0.00036	2.1198 ± 0.0015	15.520 ± 0.017	37.344 ± 0.051
152B-A			17.5833	0.0036	0.880230	0.0008	2.11612	0.0007	17.611 ± 0.011	0.88091 ± 0.00036	2.1196 ± 0.0015	15.514 ± 0.017	37.329 ± 0.051
Mean									17.614 ± 0.008	0.88096 ± 0.00026	2.1196 ± 0.0011	15.517 ± 0.012	37.336 ± 0.035
152B-B			17.8703	0.0021	0.867707	0.0008	2.09640	0.0014	17.899 ± 0.011	0.86837 ± 0.00037	2.0998 ± 0.0015	15.543 ± 0.017	37.585 ± 0.051
152B-B			17.8691	0.0043	0.867603	0.0011	2.09621	0.0021	17.898 ± 0.012	0.86827 ± 0.00036	2.0998 ± 0.0015	15.540 ± 0.017	37.579 ± 0.051
Mean									17.899 ± 0.008	0.86832 ± 0.00026	2.0997 ± 0.0010	15.542 ± 0.012	37.582 ± 0.035
152B-C			17.7565	0.0035	0.872904	0.0013	2.10490	0.0027	17.785 ± 0.011	0.87357 ± 0.00036	2.1083 ± 0.0015	15.538 ± 0.017	37.497 ± 0.051
152B-C			17.7574	0.0023	0.872922	0.0010	2.10494	0.0019	17.786 ± 0.011	0.87359 ± 0.00036	2.1084 ± 0.0015	15.538 ± 0.017	37.499 ± 0.051
Mean									17.786 ± 0.008	0.87358 ± 0.00026	2.1084 ± 0.0011	15.537 ± 0.012	37.498 ± 0.035
Mean 152A-C	1730								17.770 ± 0.355	0.87400 ± 0.01573	2.1090 ± 0.0253	15.532 ± 0.030	37.470 ± 0.307
3-12151-B		Res. Soil											
151B			18.1366	0.0037	0.856863	0.0013	2.08485	0.0026	18.168 ± 0.012	0.85752 ± 0.00037	2.0883 ± 0.0015	15.579 ± 0.017	37.939 ± 0.051
151B			18.1582	0.0037	0.857268	0.0012	2.08697	0.0023	18.187 ± 0.012	0.85792 ± 0.00037	2.0904 ± 0.0015	15.603 ± 0.018	38.018 ± 0.051
151B			18.1378	0.0024	0.856824	0.0009	2.08434	0.0017	18.167 ± 0.012	0.85746 ± 0.00037	2.0877 ± 0.0015	15.578 ± 0.017	37.928 ± 0.051
Mean	540								18.174 ± 0.024	0.85764 ± 0.00043	2.0888 ± 0.0031	15.587 ± 0.030	37.960 ± 0.106
3-12039-B		Res. Soil											
039B			18.2487	0.0033	0.852022	0.0017	2.07294	0.0034	18.278 ± 0.012	0.85268 ± 0.00037	2.0763 ± 0.0015	15.585 ± 0.017	37.951 ± 0.051
039B			18.2491	0.0022	0.851817	0.0011	2.07196	0.0020	18.278 ± 0.012	0.85247 ± 0.00037	2.0753 ± 0.0015	15.582 ± 0.017	37.934 ± 0.051
Mean	413								18.278 ± 0.008	0.85258 ± 0.00026	2.0758 ± 0.0010	15.584 ± 0.012	37.942 ± 0.036
3-12035-B		Res. Soil											
035B			18.0680	0.0028	0.860566	0.0009	2.08797	0.0020	18.097 ± 0.012	0.86123 ± 0.00037	2.0914 ± 0.0015	15.586 ± 0.017	37.848 ± 0.051
035B			18.0558	0.0038	0.860315	0.0017	2.08619	0.0032	18.085 ± 0.012	0.86097 ± 0.00037	2.0896 ± 0.0015	15.571 ± 0.017	37.790 ± 0.051
035B			18.0648	0.0039	0.860463	0.0011	2.08736	0.0010	18.094 ± 0.012	0.86112 ± 0.00037	2.0908 ± 0.0015	15.581 ± 0.017	37.830 ± 0.051
Mean	824								18.092 ± 0.007	0.86111 ± 0.00021	2.0906 ± 0.0009	15.579 ± 0.010	37.823 ± 0.029

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Table 2. Contd.

Lab No/EPA No.[3]	Pb ppm[4]	Type	Raw Data[1]						Corrected for mass fractionation[2]				
			$^{206}Pb/^{204}Pb$	% S.E.	$^{207}Pb/^{206}Pb$	% S.E.	$^{208}Pb/^{206}Pb$	% S.E.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
3-12040-B		Res. Soil											
040B			18.4206	0.0050	0.845624	0.0020	2.06295	0.0044	18.450 ± 0.012	0.84627 ± 0.00037	2.0663 ± 0.0015	15.614 ± 0.018	38.124 ± 0.052
040B			18.4169	0.0032	0.845433	0.0010	2.06280	0.0016	18.446 ± 0.012	0.84608 ± 0.00037	2.0662 ± 0.0015	15.607 ± 0.018	38.113 ± 0.052
Mean	256								18.448 ± 0.008	0.84617 ± 0.00025	2.0662 ± 0.0010	15.611 ± 0.012	38.118 ± 0.036

1 Uncertainties are in percent and represent one standard error (= 1 sigma mean).

2 Corrected for mass fractionation based on analyses of NIST standard SRM 981 (Table A1). Uncertainties are absolute and are at the 95% confidence interval (Ludwig, 1980; 1994).

3 Individual mass spectrometer runs are listed separately under the same lab sample number. Separate acid-digestions of the same sample are listed as "-A" through "-F".

4 Pb concentrations provided by USEPA from acid digestions of splits of the samples.

Color Chart(s)

The following pages contain color that does not appear in the scanned images.
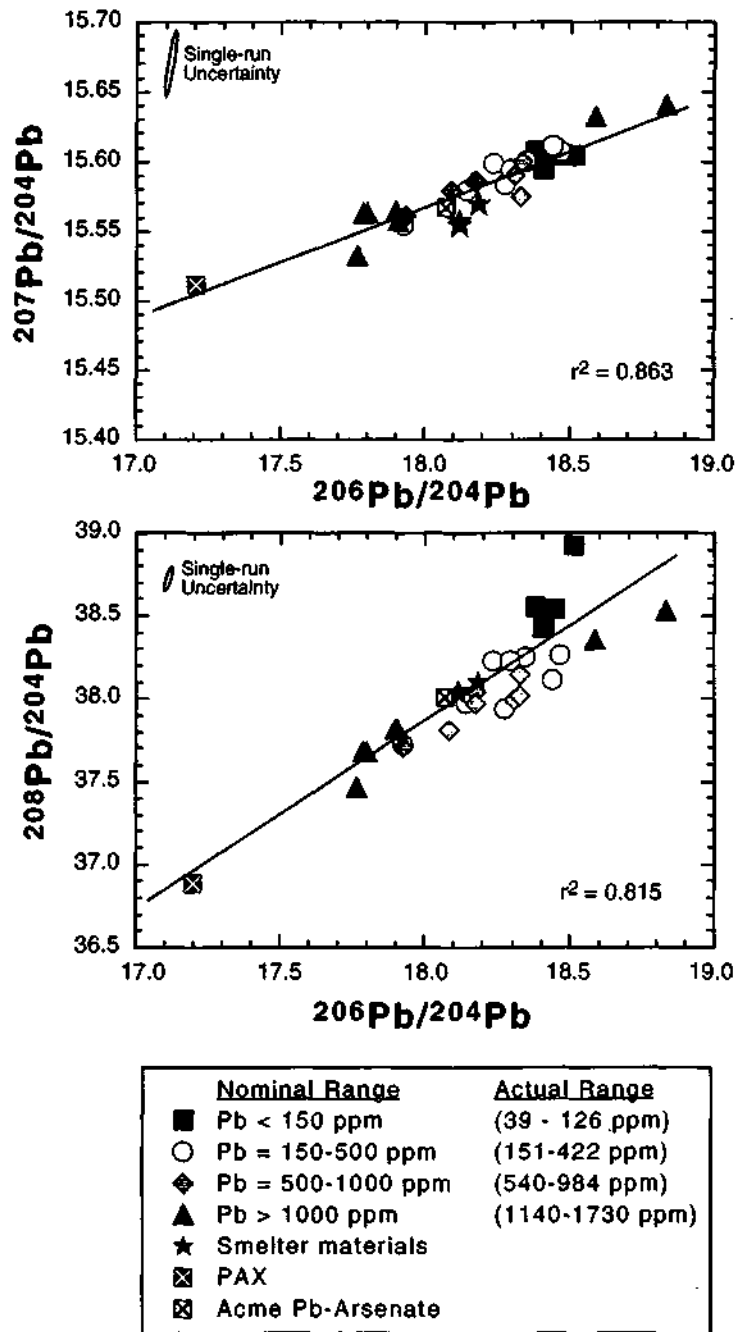
Figure 1. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams for selected soil samples from the Vasquez Blvd.-I70 study area, coded by Pb concentrations. Data are from Table 2 and represent the mean values for individual samples. Best fit lines (unweighted) through the data yield r^2 values (square of the regression correlation coefficients) of 0.863 and 0.815 for $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$, respectively. Also shown is the typical uncertainty (95% C.I.) for and individual mass spectrometer run.

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Lead isotopic data for the Acme lead arsenate, smelter soils, and smelter waste are very similar to one another and to some of the residential soils. On the other hand, the sample of PAX has a unique and nonradiogenic (low $^{206}Pb/^{204}Pb$) lead isotopic composition with $^{206}Pb/^{204}Pb = 17.21$.

The Pb isotopic compositions presented in Figure 1 are also shown in Figure 2, but the data points are coded based on As concentrations. Low-As samples are generally the most radiogenic with $^{206}Pb/^{204}Pb > 18.25$ (two exceptions, both from the same residential property). High-As samples show two distinct groups; one with $^{206}Pb/^{204}Pb < 17.9$, and one with $^{206}Pb/^{204}Pb = 18.15-18.18$. Comparison of Figures 1 and 2 reveals that the soils with high Pb and As are characterized by $^{206}Pb/^{204}Pb < 17.9$, whereas the samples with radiogenic Pb and slightly-elevated $^{208}Pb/^{204}Pb$ are low in both Pb and As.

Isotopic compositions in most of the high-As and high-Pb samples are less radiogenic than the smelter material, Acme Pb arsenate, or the low-As and low-Pb soils (baseline soils). Consequently, these soils must have a component of PAX (or some similar, but as yet unidentified material) within them. However, the isotopic data for the three contaminants and the residential soils are nearly colinear. Consequently, from the lead isotopic data alone it is not possible to determine whether the Pb in the high-As, high-Pb soils is a simple mixture of PAX and baseline soil or whether the other contaminants are also present.

Sources of Lead

Lead and As concentrations of the residential soils, coded according to their $^{206}Pb/^{204}Pb$ values, are shown in Figure 3. Shown for comparison are data from a selected number of other residential soils within the study area that were not analyzed for Pb isotopic compositions. Uncontaminated or least-contaminated samples, represented by the cluster of points with low As and Pb, have $^{208}Pb/^{204}Pb = 18.3->18.5$, although the majority of the samples have $^{208}Pb/^{204}Pb = 18.4-18.5$. The samples highest in As (>1200 ppm) are characterized by $^{208}Pb/^{204}Pb < 18.0$, even though Pb contents vary from 400 to over 1500 ppm. As mentioned above, samples with the highest Pb contents fall into two groups; one with $^{208}Pb/^{204}Pb > 18.5$ and one with $^{208}Pb/^{204}Pb < 18.0$. Both isotopic groups are found among low-As-residential soils (lower right in Figure 3). These results indicate that there are at least two high-Pb, low-As contaminants present in these soils.

Lead isotopic compositions, represented by $^{206}Pb/^{204}Pb$, are shown as a function of Pb concentration in Figure 4. Six lead sources are represented as summarized in Table 3. The uncontaminated or least-contaminated end member is defined by the low-As and low-Pb samples. This component with $^{206}Pb/^{204}Pb = 18.48$ and Pb = 70 ppm is represented by the means of the baseline soil sample, SC-00065, and the lowest-Pb sample, SC-00017.
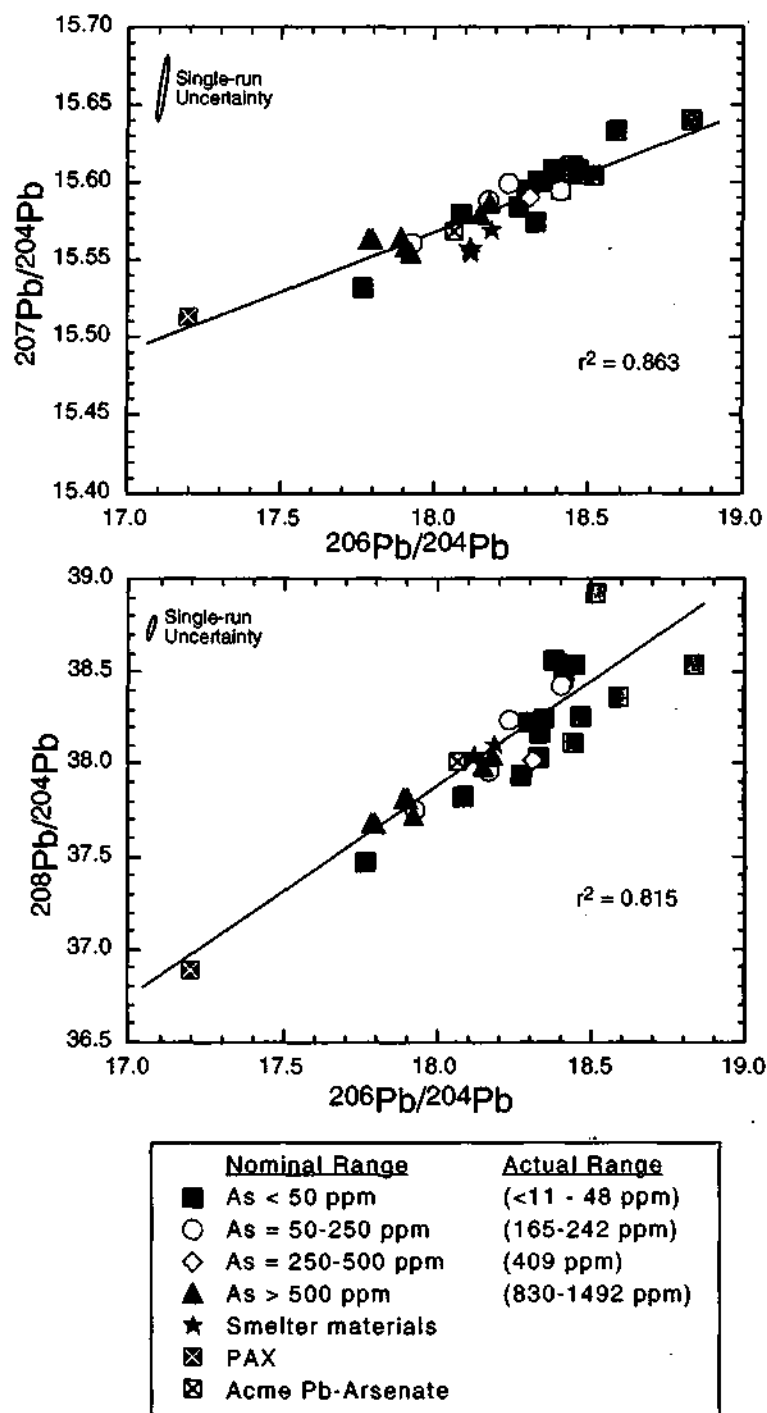
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15.70

15.65

15.60

15.55

207Pb/204Pb

15.50

15.45

15.40

Single-run
Uncertainty

$r^2 = 0.863$

17.0   17.5   18.0   18.5   19.0

206Pb/204Pb

39.0

38.5

38.0

208Pb/204Pb

37.5

37.0

36.5

Single-run
Uncertainty

$r^2 = 0.815$

17.0   17.5   18.0   18.5   19.0

206Pb/204Pb

Nominal Range	Actual Range
■ As < 50 ppm	(<11 - 48 ppm)
○ As = 50-250 ppm	(165-242 ppm)
◇ As = 250-500 ppm	(409 ppm)
▲ As > 500 ppm	(830-1492 ppm)
★ Smelter materials	
⊠ PAX	
⊠ Acme Pb-Arsenate	

Figure 2. 206Pb/204Pb vs. 207Pb/204Pb and 206Pb/204Pb vs. 208Pb/204Pb diagrams for selected soil samples from the Vasquez Blvd.-I70 study area, coded by As concentrations. Data are from Table 2 and represent the mean values for individual samples. Also shown are the typical uncertainty (95% C.I.) for and individual mass spectrometer run and best-fit lines through all of the data.
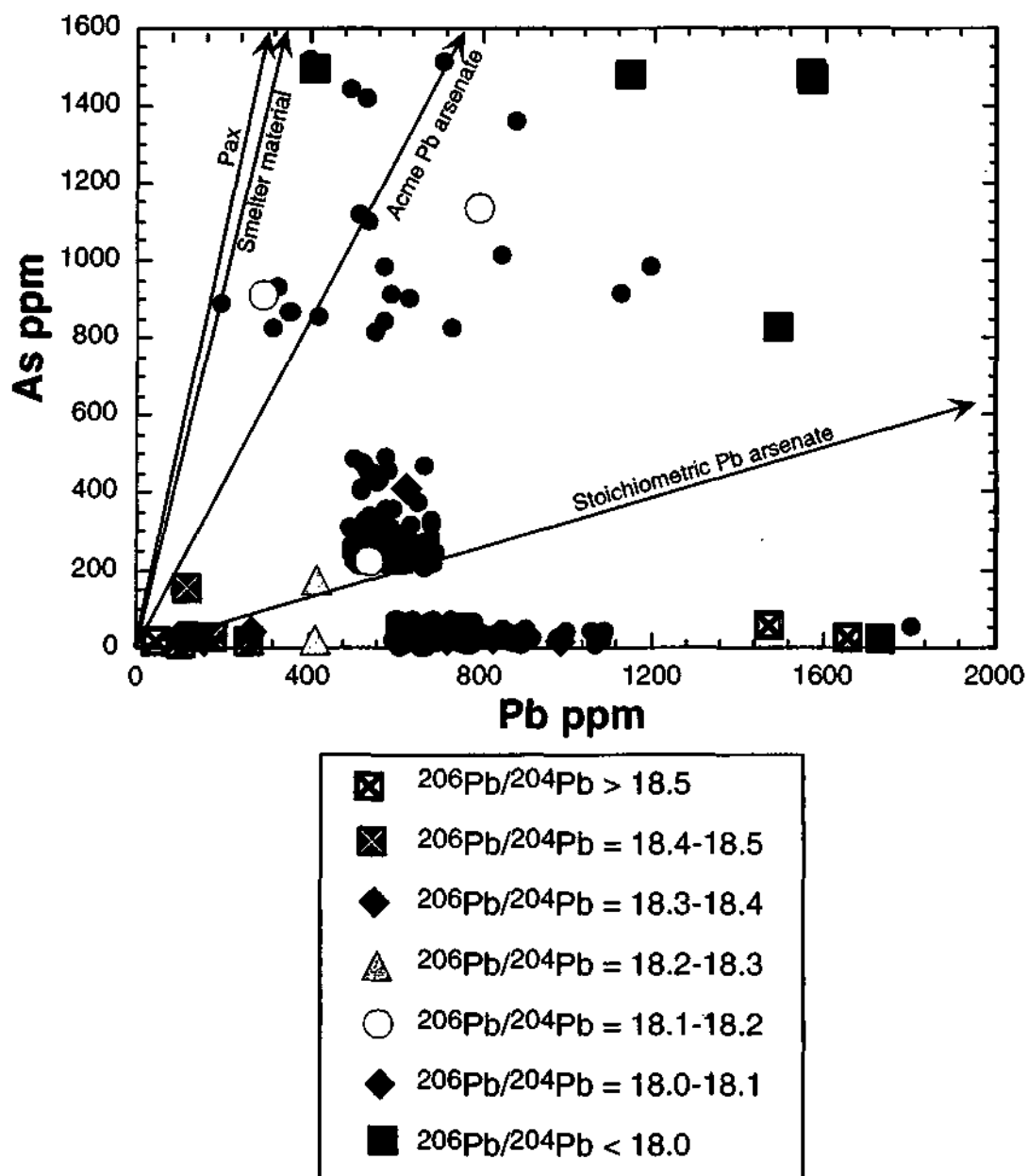
Figure 3. As vs. Pb concentrations for selected samples from the VBI70 study area. Samples are coded according to their $^{206}Pb/^{204}Pb$ values. Also shown by the small filled circles are data from samples not analyzed for Pb isotopic compositions? Vectors for PAX, smelter soils and materials, Acme lead arsenate, and stoichiometric Pb arsenate ($PbAsO_4$), which are all off the scale of the diagram, are also shown.

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Table 3. Summary of identified Pb sources in the VBI70 study area.

Sample	Type	Pb ppm	As ppm	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Baseline						
Mean[1]	res soils.	70	8	18.476	15.604	38.732
High-As contaminants						
3-15639-B	Acme Pb-Arsenate	128000	273000	18.071	15.568	38.009
3-15658-B	PAX	24300	120000	17.206	15.513	36.886
3-15643-B	Smelter-soil	4520	22400	18.190	15.570	38.101
3-15645-B	Smelter-soil	5660	27200	18.122	15.557	38.026
3-15646-B	Smelter-material	2160	7630	18.121	15.554	38.035
Mean smelter materials & soils		4113	19077	18.144	15.560	38.054
Low-As contaminants[2]						
3-10319-B	res. soil	1469	48	18.837	15.641	38.534
3-12152-B	res. soil	1730	<11	17.770	15.532	37.470

[1] Mean of soils 3-15644-B and 3-15654-B

[2] The residential soils with highest lead contents are used to approximate the contaminants. The true contaminant should have higher Pb concentrations and slightly different lead isotopic values.

The data for the PAX sample represent one possible contaminant with $^{206}Pb/^{204}Pb$ = 17.21 and Pb = 24300 ppm. A second contaminant is represented by the lead arsenate sample with $^{206}Pb/^{204}Pb$ = 18.07 and Pb = 128000 ppm. The smelter soils with $^{206}Pb/^{204}Pb$ ≈ 18.12-18.19 and Pb ≈ 2160-5600 ppm represent a third contaminant source. Each of these three sources represents a potential As as well as Pb contaminant.

Two additional contaminants are approximated by residential soils 3-10319-B and 3-12152-B. These sources appear to represent Pb contamination, but not As. Because these soils are likely mixtures of contaminant and baseline material, the actual Pb concentrations in the true contaminants are probably higher than in the soils and the Pb isotopic compositions more extreme ($^{206}Pb/^{204}Pb$ ≥ 18.84 and ≤17.77 for 3-10319-B and 3-12152-B, respectively). Another high-Pb sample with $^{206}Pb/^{204}Pb$ = 18.6 may reflect yet another Pb contaminant or a mixture of Pb contaminants.

Two-Component Mixing

Calculated bulk-mixing curves between average baseline and each of the five-contaminant sources are shown for reference in Figure 4A. The bulk mixing curves are calculated from the following two-component bulk-mixing equations (Faure, 1977):

(1) $$C_M = C_C * (X) + C_B * (1-X)$$

(2) $$R_M = [R_C * C_C *(X) + R_B * C_B * (1-X)] / C_M$$

where C_C, and C_B are the concentrations of an element, in this case lead, in the contaminant (C) and baseline (B); C_M is the concentration of the element in the mixture (a contaminated soil sample), and X is the weight fraction of contaminant source A in the mixture (where $0 \leq X \leq 1$). R_A, R_B, and R_M are the isotopic ratios (in this case $^{206}Pb/^{204}Pb$) in the contaminant source, baseline, and mixture, respectively. The percent contamination is 100*X. The weight fraction of an element in a soil, X_C, derived from the contaminant is calculated from X in the following manner (Church and others, 2002):

(3) $$X_C = X*C_C/C_M$$

By combining equations (1) and (2) and eliminating X, the following expression is obtained (Faure, 1977):

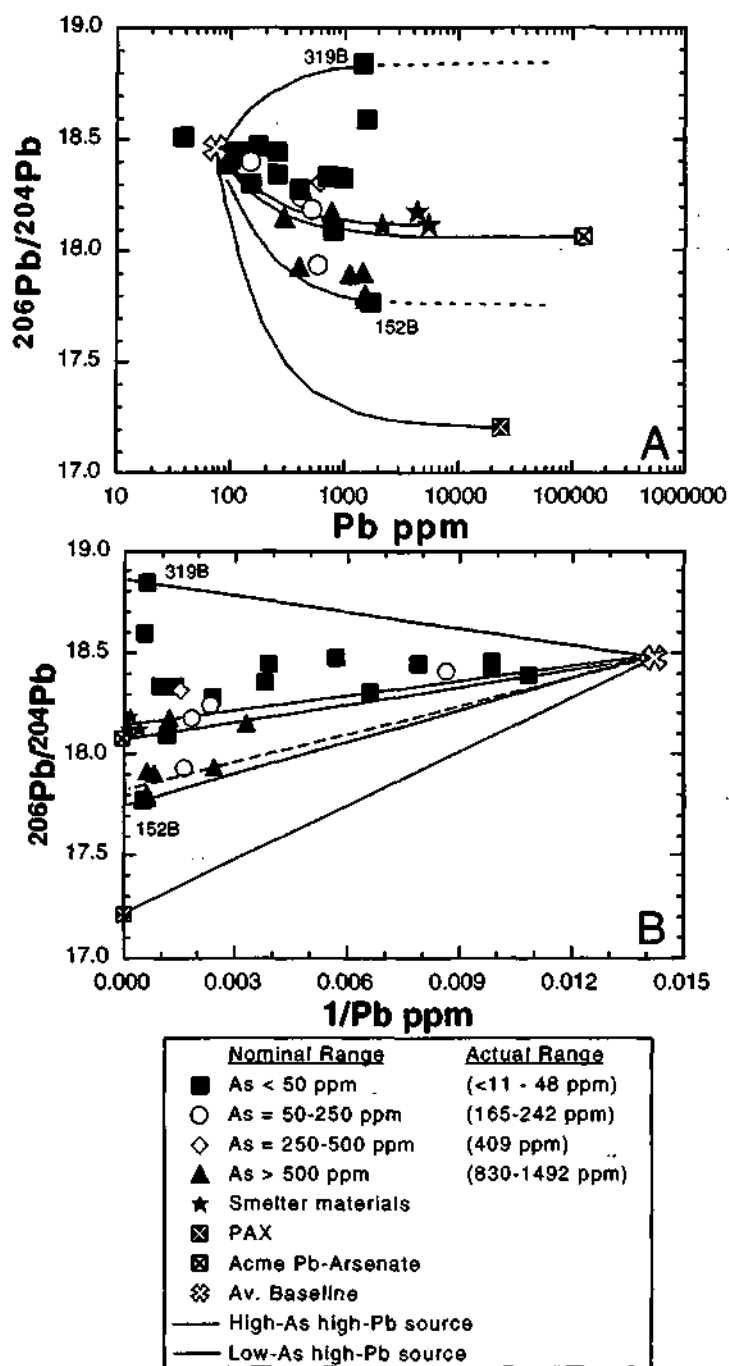(4) $$R_M = [C_C *C_B * (R_C - R_B)]/ [C_M *(C_C - C_B)] + (C_C * R_A - C_B * R_B) / (C_C - C_B)$$

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Figure 4. (A) $^{206}Pb/^{204}Pb$ vs. Pb concentration and (B) $^{206}Pb/^{204}Pb$ vs. 1/Pb concentration for selected soil samples from the VBI70 study area. Data are from Table 2 and represent the grand means of data from individual samples (bold type in Table 2). An average baseline value (cross, $^{206}Pb/^{204}Pb$ = 18.48, Pb = 70 ppm) is estimated from data for samples 3-15654-B and 3-15644-B. Bulk-mixing curves (lines in Figure 4B) between average baseline and PAX, smelter soil, Acme lead arsenate, soil 3-10319-B (319B), and soil 3-12152-B (152B) are shown for reference. The broken line in Figure 4B represents a hypothetical mixing line between average baseline and a Pb + As source with 206Pb/204Pb 17.8.

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This equation is of the general form:

$$R_M = a / C_M + b$$

which is the form for a hyperbolic curve when R_M is plotted as a function of C_M (a and b are constants dependent upon the values of C_C, C_B, R_C, and R_B). The mixing hyperbole is converted to a straight line if R_M is plotted as a function of $(1/C_M)$ as is shown in Figure 4B.

Four points regarding Figure 4 are worthy of mention. (1) The bulk mixing curves for Acme lead arsenate and average smelter material are nearly superimposed upon one another. This means that the Pb data are not able to resolve contamination from these two sources. (2) Most of the low-As samples plot above the mixing curves for lead arsenate and smelter material. This observation coupled with the fact that these samples show a wide range in lead contents indicates that Pb contamination from a source or sources with radiogenic Pb ($^{206}Pb/^{204}Pb > 18.2$) is common among the low-As soils. One might reasonably conclude that this contamination is also present among the higher-As soils as well, but may be masked by other contaminants. (3) The data for many of the high-As residential samples plot between the PAX and lead arsenate - smelter material mixing curves. This suggests that the Pb in these samples was derived from at least three sources: baseline, PAX and at least one other contaminant source. Alternatively, the results may indicate the presence of another contaminant with $^{206}Pb/^{204}Pb \approx 17.8$, similar to soil 3-12152-B, but with high As as well as Pb (broken red line in Figure 4B). (4) Finally, data for two of the high-As soils (3-13989-B and 3-12524-B) as well as three of the intermediate-As soils (3-15648-B, 3-15642-B, and 3-12151-B) plot on or near the mixing lines (Figure 4B) between baseline and smelter material or lead arsenate. This suggests that lead arsenate or smelter material may represent the principal contaminant in these samples. However, if multiple contaminants are involved, then the position of these data relative to the lead arsenate and smelter material mixing curves may be fortuitous.

In a situation involving two-component-mixing, the weight fraction of contaminant (X) can be semi-independently calculated from both equations 1 and 2 (equations 1 and 2 are not totally independent because the concentration data are used in both equations). The weight fraction of contaminant Pb, X_{Pb}, in a sample can also be estimated using the Pb isotopic compositions alone (Church and others, 1997; 2002) as follows:

(5) $$X_{Pb} = (R_M - R_B)/(R_C - R_B)$$

Table 4. Two-component mixing parameters for selected soil samples from the VBI70 study area.

Components	Sample	Pb ppm	As ppm	$^{206}Pb/^{204}Pb$	$X_c Pb^1$	X_{Pb}^2	X Pb (1)[3]	X Pb (2)[4]	X Pb (6)[5]	X As (1)[3]
Acme Pb arsenate	3-13989-B	302	904	18.150	0.769	0.805	0.0018	0.0018	0.0019	0.0033
and average baseline	3-12524-B	794	1135	18.181	0.912	0.728	0.0057	0.0057	0.0045	0.0041
	3-15648-B	115	165	18.410	0.392	0.163	0.0004	0.0004	0.0002	0.0006
	3-15642-B	422	173	18.242	0.835	0.578	0.0028	0.0028	0.0019	0.0006
	3-12151-B	540	221	18.174	0.871	0.746	0.0037	0.0037	0.0032	0.0008
Average smelter material	3-13989-B	302	904	18.150	0.782	0.982	0.0574	0.0571	0.0721	0.0470
and average baseline	3-12524-B	794	1135	18.181	0.928	0.889	0.1791	0.1792	0.1715	0.0591
	3-15648-B	115	165	18.410	0.398	0.199	0.0111	0.0112	0.0056	0.0082
	3-15642-B	422	173	18.242	0.849	0.705	0.0871	0.0873	0.0723	0.0087
	3-12151-B	540	221	18.174	0.885	0.910	0.1163	0.1162	0.1194	0.0112

[1]Weight fraction of contaminant Pb in the soil calculated from Pb concentrations using equation (3).

[2]Weight fraction of contaminant Pb in the soil calculated from Pb isotopic compositions using equation (5).

[3]Weight fraction of contaminant in the soil calculated from Pb or As concentrations using equation (1).

[4]Weight fraction of contaminant in the soil calculated from equation (2).

[5]Weight fraction of contaminant in the soil calculated from equation (6).

The weight fraction of contaminant, X, can then be calculated from X_{Pb} and the Pb concentrations in the contaminant and soil in the following manner:

$$(6) \qquad X = X_{Pb} * C_M/C_C$$

Equations (3) and (5) provide two independent methods of estimating the relative amount of contaminant Pb within a soil, one based solely on the Pb concentrations (3), and one based exclusively on the Pb isotopic compositions (5). Equation (6) also provides another semi-independent method of estimating the relative amount of contaminant in a soil. The As concentration data can also be used in equation (1) to provide an independent check of the calculations.

Two-component mixing calculations for the five soils mentioned above, that plot near the baseline-Pb arsenate or smelter material mixing curves, are presented in Table 4. Two sets of calculations have been made for mixing between baseline and lead arsenate and between baseline and average smelter material. It should be emphasized that these calculations represent possible solutions only. Independent verification from geochemical analyses and speciation studies are also required in order to determine whether these possible solutions are in fact reasonable. Calculations in Table 4 are highlighted in bold type when agreement among the three calculations was within a factor of 2 (arbitrary).

Data for the two high-As samples are consistent contamination of baseline soil with 0.2-0.6% acme lead arsenate. One of these samples, 3-13989-B is also consistent with contamination of baseline soil with 5-6% smelter material. Calculations for the intermediate-As sample 3-15648-B are also consistent with a small amount of contamination from either Pb arsenate or smelter material. Internally consistent results were not obtained for the other samples.

Three-Component Mixing

As mentioned above four of the six high-As samples (samples 3-15650-B and 3-15651-B are duplicate splits of the same soil) and one of the intermediate-As soils plot between the three high-As mixing curves in Figure 4. Although these samples plot close to the mixing curve for baseline and soil 3-12152-B, this soil can not represent the only contaminant in these samples because soil 3-12152-B has low As. Barring the existence of an unidentified high-As contaminant with $^{206}Pb/^{204}Pb \approx 17.8$, the Pb data for these samples must reflect contamination from more than one source.

If two contaminant sources are involved then a three-component mixing model may be employed where

$$(7) \qquad C_M = C_{C1} * (X) + C_{C2} * (Y) + C_B * (1-X-Y)$$

$$(8) \qquad R_M = [R_{C1} * C_{C1} *(X) + R_{C2} * C_{C2} *(Y) + R_B * C_B * (1-X-Y)] / C_M$$

where X and Y are the weight fractions of contaminants C1 and C2, respectively. Equations 7 and 8 may be combined to solve for both X and Y. If more than two contaminant sources are involved, then additional data are required in order to obtain unique solutions.

Three-component mixing calculations for all six high-As and all five intermediate-As soils are summarized in Table 5. All calculations are made assuming the soils are mixtures of baseline material and two contaminants. The requirements for selecting pairs of contaminants are (1) that one of the contaminants must have nonradiogenic Pb (either PAX or soil 3-12152-B; this requirement is strictly valid only for those soils having $^{206}Pb/^{204}Pb < 18.08$) and (2) that at least one of the contaminants must have high As (either PAX, lead arsenate, or smelter material). Using these criteria, 5 different situations are allowed (Table 5). Weight fractions of the two contaminants were calculated using the Pb concentration and Pb isotopic data in equations 4 and 5. Arsenic contents were calculated from these proportions and arsenic contents of the contaminants using equation 4. The calculated arsenic contents are compared to the measured As in the soils in Table 5. Calculations highlighted in bold are for calculated As contents that are within a factor of 2 of the measured values. Once again, the calculations only indicate possible solutions which must be used in conjunction with other evidence.

Consistent results were not obtained. Data for some samples (e.g. 3-13569-B and 3-13989-B) have multiple solutions whereas data for other samples (3-15650-B and 3-00748-B) yield no satisfactory solutions. If taken at face value, the data in Table 5 suggest that the As and Pb contamination in each residential property is derived from a unique set of circumstances.

The calculations in Tables 4 and 5 are complicated by several factors. First, the proportions of lead and arsenic currently present in the soils may be different from those in the potential sources as a result of preferential dissolution of specific chemical phases from the soils (J. Drexler, oral communication, 2001). Second, the smelter soils present today may have different chemical and isotopic signatures from soils present in the past. This is particularly true of the smelter in question, which switched from arsenic to cadmium refining during the late 1920's. It should also be noted that two other smelters were at one time present in this general area, but samples from these smelters are not available. Finally, the samples of PAX and lead arsenate represent only two of several similar compounds that might have been commercially available during the middle 20th century. The proportions of lead and arsenic as well as the lead isotopic signatures of this other material, or of the PAX and Acme lead arsenate for that

Table 5. Three-component mixing calculations for selected resedential soils from the VBI70 study area.[1]

Sample	Pb ppm	$^{206}Pb/^{204}Pb$	% Cont. C_1[2]	% Cont. C_2[3]	Calc. As ppm[4]	Meas. As ppm
Contaminants: Pax and Acme Pb arsenate						
	Pb ppm	$^{206}Pb/^{204}Pb$	% PAX	% Acme	Calc. As ppm	Meas. As ppm
3-15641-B	1490	17.910	1.27	0.87	3908	836
3-15650-B	1560	17.801	2.13	0.76	4645	1490
3-15657-B	1140	17.898	1.07	0.63	3023	1490
3-13569-B	409	17.930	0.41	0.19	1010	1492
3-13989-B	302	18.150	0.02	0.18	517	904
3-12524-B	794	18.181	-0.28	0.62	1361	1135
3-15648-B	115	18.410	-0.05	0.04	70	165
3-15642-B	422	18.242	-0.21	0.31	617	173
3-12820-B	607	17.936	0.52	0.32	1511	242
3-12151-B	540	18.174	-0.13	0.39	922	221
3-00748-B	633	18.316	-0.60	0.55	798	409
Contaminants: Pax and average smelter material						
	Pb ppm	$^{206}Pb/^{204}Pb$	% PAX	% smelter	Calc. As ppm	Meas. As ppm
3-15641-B	1490	17.910	1.60	25.51	6797	836
3-15650-B	1560	17.801	2.42	22.33	7174	1490
3-15657-B	1140	17.898	1.31	18.60	5130	1490
3-13569-B	409	17.930	0.48	5.51	1634	1492
3-13989-B	302	18.150	0.09	5.21	1107	904
3-12524-B	794	18.181	-0.05	18.18	3420	1135
3-15648-B	115	18.410	-0.03	1.31	218	165
3-15642-B	422	18.242	-0.09	9.24	1663	173
3-12820-B	607	17.936	0.65	9.41	2578	242
3-12151-B	540	18.174	0.02	11.51	2226	221
3-00748-B	633	18.316	-0.39	16.27	2641	409
Contaminants: soil 3-12152-B and Acme lead arsenate						
	Pb ppm	$^{206}Pb/^{204}Pb$	% 152-B	% Acme	Calc. As ppm	Meas. As ppm
3-15641-B	1490	17.910	48.83	0.48	1310	836
3-15650-B	1560	17.801	81.87	0.10	289	1490
3-15657-B	1140	17.898	41.07	0.30	837	1490
3-13569-B	409	17.930	15.66	0.06	177	1492
3-13989-B	302	18.150	0.81	0.17	474	904
3-12524-B	794	18.181	-10.78	0.71	1935	1135
3-15648-B	115	18.410	-1.94	0.06	173	165
3-15642-B	422	18.242	-8.00	0.38	1042	173
3-12820-B	607	17.936	20.08	0.16	443	242
3-12151-B	540	18.174	-4.99	0.43	1188	221
3-00748-B	633	18.316	-23.12	0.74	2028	409

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Table 5. Cont'd.

Sample	Pb ppm	$^{206}Pb/^{204}Pb$	% Cont. C_1[2]	% Cont. C_2[3]	Calc. As ppm[4]	Meas. As ppm

Contaminants: Soil 12152-B and average smelter material

Sample	Pb ppm	$^{206}Pb/^{204}Pb$	% 152-B	% smelter	Calc. As ppm	Meas. As ppm
3-15641-B	1490	17.910	55.05	12.52	2396	836
3-15650-B	1560	17.801	83.21	2.69	523	1490
3-15657-B	**1140**	**17.898**	**45.03**	**7.98**	**1530**	**1490**
3-13569-B	409	17.930	16.47	1.62	318	1492
3-13989-B	**302**	**18.150**	**3.04**	**4.49**	**864**	**904**
3-12524-B	794	18.181	-1.56	18.55	3545	1135
3-15648-B	115	18.410	-1.15	1.59	310	165
3-15642-B	422	18.242	-3.05	9.96	1907	173
3-12820-B	607	17.936	22.16	4.18	806	242
3-12151-B	540	18.174	0.66	11.36	2173	221
3-00748-B	633	18.316	-13.45	19.45	3716	409

Contaminants: PAX and soil 3-10319-B

Sample	Pb ppm	$^{206}Pb/^{204}Pb$	% PAX	% 319-B	Calc. As ppm	Meas. As ppm
3-15641-B	1490	17.910	3.45	41.75	4165	836
3-15650-B	1560	17.801	4.04	36.54	4870	1490
3-15657-B	1140	17.898	2.66	30.44	3210	1490
3-13569-B	**409**	**17.930**	**0.88**	**9.02**	**1066**	**1492**
3-13989-B	**302**	**18.150**	**0.47**	**8.52**	**570**	**904**
3-12524-B	**794**	**18.181**	**1.27**	**29.75**	**1544**	**1135**
3-15648-B	**115**	**18.410**	**0.06**	**2.15**	**83**	**165**
3-15642-B	422	18.242	0.58	15.12	710	173
3-12820-B	607	17.936	1.33	15.40	1606	242
3-12151-B	540	18.174	0.85	18.84	1038	221
3-00748-B	633	18.316	0.79	26.63	962	409

[1]Calculations in bold represent agreement to within a factor of 2 for calculated vs. measured As contents.
and no significant significant negative contribution from one of the contaminant sources.

[2] X (*100) calculated from simultaneous solutions of equations 7 and 8.

[3] Y (*100) calculated from simultaneous solutions of equations 7 and 8.

[4] As concentration calculated from equation 7 and X and Y values calculated for Pb.

matter, may have been different from those observed in the existing samples depending upon the sources of lead used in the manufacture of the products.

Focal versus Adjacent Samples

Samples of residential soils adjacent to high- and intermediate-As soils have been analyzed (Table 1) in order to determine whether significant migration of Pb or As from the high-As properties has occurred. All of the adjacent samples analyzed in this study have <50 ppm As (Table 1) which suggests that As migration to surrounding properties has been minimal.

Pb isotopic compositions of the soil samples, this time coded by sample type, are shown in Figure 5. Low-As focal samples, which show large variations in Pb contents (Table 1), span almost the entire range of isotopic values found within the residential soils. The single low-As adjacent sample analyzed has the highest $^{208}Pb/^{204}Pb$ and among the highest $^{206}Pb/^{204}Pb$. Data for the two high-As adjacent samples and the single intermediate-As adjacent samples are well within the range observed for other low-As (focal) samples, although the $^{206}Pb/^{204}Pb$ values for the high-As adjacent samples are slightly less radiogenic than those in the low-As and intermediate-As adjacent samples.

Lead contents of the high-As adjacent samples are significantly higher than baseline values (150-260 ppm versus ≈70 ppm; Tables 1 and 3), but are well within the range of other low-As samples (Figure 6). However, the $^{206}Pb/^{204}Pb$ values in these two samples appear to be slightly lower than in other low-As samples with similar Pb contents. The data are therefore consistent with the interpretation that some migration of non-radiogenic Pb has occurred from the high-As properties to the surrounding properties.

Samples from a Single Property

Five samples, 3-12152-B, 3-12151-B, 3-12040-B, 3-12039-B, and 3-12035-B (Table 2), were collected from a single residential property in order to look at mixing relationships within a geographically restricted area. The samples show a wide range in Pb contents, 256-1730 ppm Pb. Four of the five samples have As < 50 ppm, but sample 3-12151-B has 221 ppm As. Sample 3-12152-B represents the low-As contaminant source with nonradiogenic Pb (Table 3).

Lead isotopic data for the five sediments are highly correlated with r^2 values of 0.947 and 0.961 for the $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams, respectively (Figure 7). The high degree of correlation suggests that the data are best
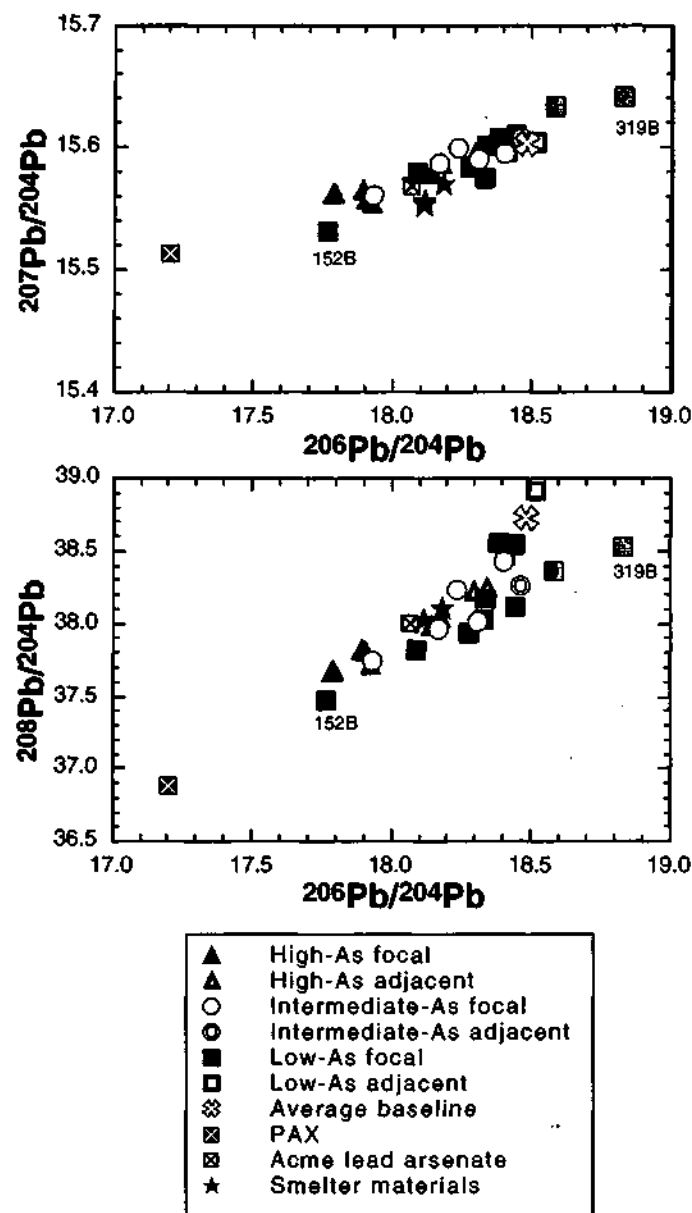
29

Figure 5. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams for focal vs. adjacent samples from the VBI70 study area. Samples are coded by As concentrations. Focal samples are shown by filled symbols and adjacent samples by open symbols.
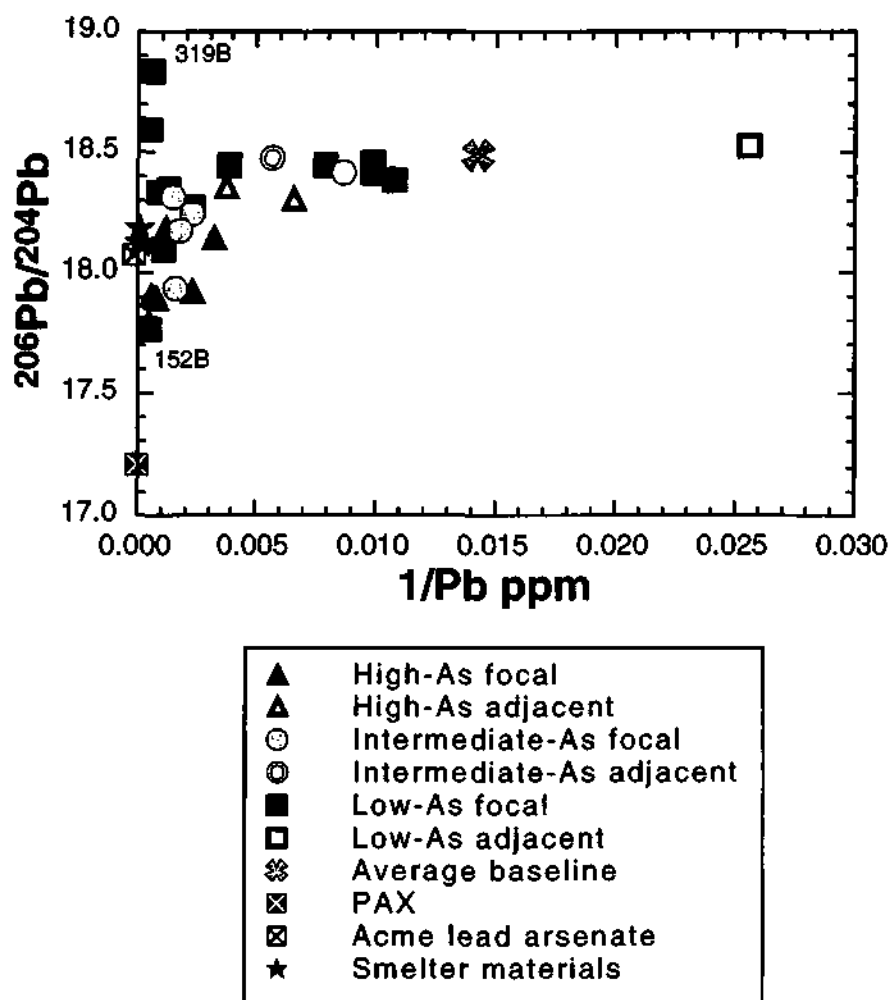
Figure 6. $^{206}Pb/^{204}Pb$ vs. 1/Pb concentrations for focal vs. adjacent samples from VBI70 study area. Samples are coded by As concentrations.

explained in terms of mixing between two components. However, the best-fit line on the $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagram does not pass through the average baseline value.

The $^{206}Pb/^{204}Pb$ values are shown as a function of Pb contents (1/Pb) in Figure 8. The data are moderately well correlated with $r^2 = 0.884$, but there is obvious scatter about the best-fit line, and the best-fit line passes nowhere near the average baseline value. The results again suggest that there are at least two Pb components in these soils. One of the components has isotopic characteristics similar to soils 3-12152-B ($^{206}Pb/^{204}Pb \approx 17.8$, Pb ≥ 1730 ppm). The other has $^{206}Pb/^{204}Pb \geq 18.45$ but Pb ≤ 256 ppm.

The high lead component is clearly a contaminant, but the nature of the other end member is somewhat problematic. The trend may suggest that baseline isotopic ratios in this soil are much more radiogenic than in other low-As soils (the baseline values lie on the upper right extension of the mixing line in Figure 8).

Another way in which low-Pb end-member could be explained is that this end member is a mixture between baseline Pb and a second contaminant with radiogenic Pb. If the two contaminants (i.e. those represented by soils 3-12152-B and 3-10319-B) were randomly distributed within the soils at this property, then a linear trend in Figure 8 would not be expected. The data would simply fall anywhere within an envelope defined by average baseline and soils 3-12152-B and 3-10319-B. The fact that a scattered linear trend does exist may suggest that variable amounts of contamination from the source represented by soil 3-12152-B were superimposed onto a soil that was more or less uniformly contaminated by the radiogenic -Pb contaminant.

The presence of two contaminants is consistent with the results from multiple acid-digestions of sample 3-12152-B (Tables 2 and A2-4). There is more isotopic variation among the replicate digestions than is easily accounted for if only a single contaminant is involved. The isotopic variation may suggest that one of the contaminants is not being totally dissolved by the acid-digestion procedure or that one of the contaminants is heterogeneously distributed within the soil at a scale comparable to the sample sizes.

The elevated As content found in sample 3-12151-B is not accounted for by either of the scenarios outlined above. This sample is intermediate in terms of both Pb contents and isotopic compositions, but has As contents almost an order of magnitude higher than in any of the other soils from this property. These observations suggest that yet another contaminant is present in this soil. Although the nature of this contaminant can not be determined, it must have very high As/Pb such that addition of this material does not significantly affect relationships between Pb concentrations and Pb isotopic compositions in Figure 8.

The results from soils from this property and the fact that there is such a large range in Pb contents among low-As soils in general (Figure 4) clearly indicate that the Pb and As
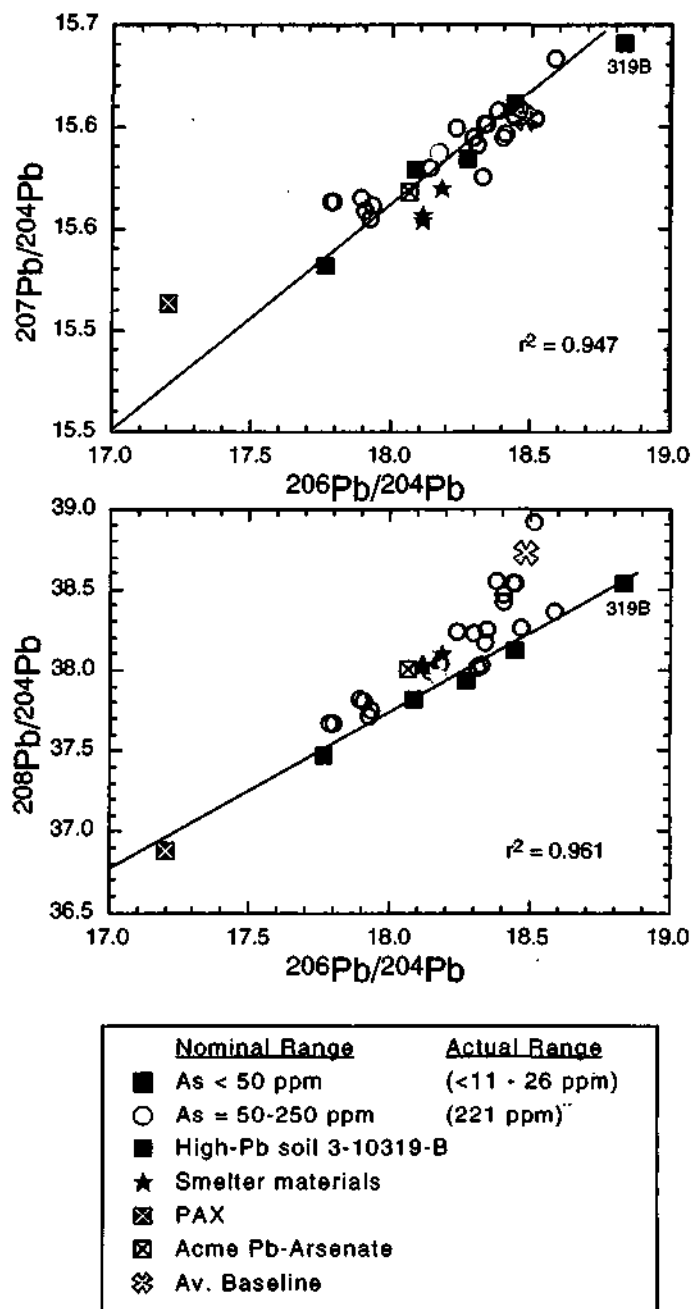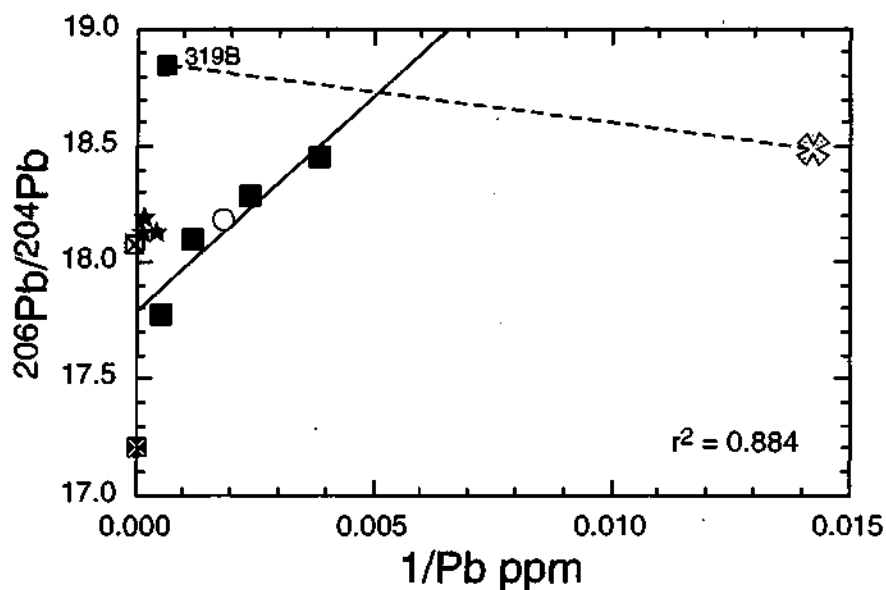
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Figure 7. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams for samples from a single residential property. Samples from the property are coded by As concentrations. Other samples from the VBI70 study area are shown for reference by open circles. Best-fit lines through the five points yield good linear arrays with $r^2 = 0.947$ and 0.961 for $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ diagrams, respectively.

Figure 8. $^{206}Pb/^{204}Pb$ vs. 1/Pb concentrations for samples from
a single residential property. Samples from the property are
coded by As concentrations. The five points determine a moder-
ately well correlated linear array with r^2 = 0.884. The broken line
represents mixing between average baseline soil and soil 3-
10319-B (319B).

contamination in the soils are not entirely related to the same sources. However, the absence or at least paucity of high-As, low-Pb soils within the sample set (Figure 1), the nonradiogenic character of the Pb in many of the high-As samples, and the presence of significant amounts of Pb arsenate in many of the soils (Laboratory for Environmental and Geochemical Studies, 2001) suggest that there are high-Pb+As sources responsible for much of the As contamination in these soils. Identification of the exact number and nature of the contaminants within these soils must await detailed studies of individual properties.

Conclusions

(1) At least six potential sources of lead have been found in selected soil samples from the Vasquez Blvd.-I70 study area based on the relationships between the isotopic compositions and Pb concentrations in the soils: (1) an average "baseline" soil with $^{206}Pb/^{204}Pb$ ≈ 18.48 and Pb ≈ 70 ppm, (2) smelter soil and waste with $^{206}Pb/^{204}Pb$ = 18.12-18.19 and Pb = 2100-5600 ppm, (3) PAX, a commercial herbicide, with $^{206}Pb/^{204}Pb$ = 17.2 and Pb = 24300 ppm, (4) Acme brand lead arsenate pesticide with $^{206}Pb/^{204}Pb$ = 18.07 and Pb = 128000 ppm, (5) an unidentified contaminant with $^{206}Pb/^{204}Pb$ ≥ 18.8 inferred from residential soil 3-10319-B, and (6) an unidentified contaminant with $^{206}Pb/^{204}Pb$ ≤ 17.8 inferred from residential soil 3-12152-B. Sources 2,3, and 4 are Pb and As contaminants whereas sources 5 and 6 appear to be Pb contaminants only.

(2) The isotopic compositions of the smelter materials and the Acme lead arsenate are similar enough that it is not possible to distinguish between these two sources as potential Pb contaminants.

(3) The Pb isotopic data for two of the high-As soils (3-13989-B and 3-12524-B) are consistent with the interpretation that they represent contamination of average baseline soil with small amounts of either Acme lead arsenate or smelter material. Confirmation of this interpretation must await detailed geochemical analyses and speciation studies of these soils.

(4) The other high-As soils (3-15641, 3-15650-B, 3-15657-B, and 3-13569-B) and one intermediate-As soil (3-12820) have $^{206}Pb/^{204}Pb$ values lower than those found in either the smelter materials or Acme lead arsenate. These samples must have within them a component of PAX (or a similarly nonradiogenic Pb-rich material). However, the Pb data for these samples cannot be explained by simple two-component mixing involving contamination of baseline soil with PAX. These data may reflect the presence of more than one Pb

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contaminant or the presence of an as yet unidentified Pb and As contaminant with $^{206}Pb/^{204}Pb \approx$ 17.8.

(5) The Pb and As data for the intermediate- and high-As soils are reasonably consistent with three-component mixing models involving baseline soil and two contaminants (Table 5). However, different contaminants are required for each of the soils and unique solutions were not obtained for most of the soils. The presence of smelter material or Acme lead arsenate in these soils are neither eliminated nor required by the calculations.

(6) Low-As soils show a wide range in Pb concentrations (39-1730 ppm) and isotopic compositions ($^{206}Pb/^{204}Pb$ = 17.8-18.8). These results clearly indicate that Pb and As contamination is at least partially decoupled within these soils. Furthermore, if such large and variable amounts of Pb-only contamination are found in the low-As samples, one might logically conclude that this type of Pb-only contamination is also present in intermediate- and high-As soils. If true, then the two-component mixing calculations involving average baseline Pb would not necessarily be valid.

(7) Analyses of soils adjacent to high-As soils are consistent with some migration of Pb from the high-As, high-Pb soils to the surrounding properties. However, given the wide variation in Pb contents and isotopic compositions found among low As focal soils, the evidence for Pb migration should be regarded as tentative.

(8) Analyses of five soils from a single residential property confirm the complex nature of the contamination in these soils. The Pb concentration and isotopic data require either the presence of two Pb contaminants or a single contaminant and unusual "baseline" with an elevated Pb concentration and/or $^{206}Pb/^{204}Pb$. In addition a third contaminant with high As and low Pb is required to account for the As content in one of the five soils from this property.

Suggestions for Future Work

Based upon the preceding discussion, it is quite evident that Pb and As contamination in these soils is a complex issue. In some instances Pb and As contamination appear unrelated whereas in other instances there is good evidence for a single principal Pb and As contaminant. Furthermore, at least 5 potential Pb contaminants and three potential As contaminants have been identified. Although the presence of PAX in four of the 6 high-As samples is indicated by the data, unique solutions could not be obtained regarding the involvement of other potential Pb and As sources.

Detailed studies of soils from individual properties, such as that represented by Figures 7 and 8 should be performed. This procedure is based on the *assumption* that individual

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properties would represent less complex systems than the study area as a whole. That is, only a restricted number of contaminants would be present at any one property. Five to six samples would generally be required and the samples would have to show a significant range in Pb (and ideally As) concentrations. Ideally, Pb and As contents should show a good correlation among the soils from a single property. The Pb data for each individual property would be plotted as in Figures 4, 6, and 8 and the data evaluated as outlined below.

(1) The data define no linear trend on a plot of $^{206}Pb/^{204}Pb$ vs. 1/Pb ppm. This would mean that multiple Pb contaminants are present and are not homogeneously distributed within the soils. In this situation it may not be possible to use Pb isotopic data to identify the source(s) of As or Pb contamination.

(2) The data define a linear trend, but there is no correlation with As contents in the samples. This is the situation observed for the samples in Figure 8 and would indicate that Pb and As are derived from separate sources. The Pb isotopic data for these samples would therefore not be a valid tool for evaluating the source of the As contamination. However, the intersection of the mixing trend with the Y-axis would define the $^{206}Pb/^{204}Pb$ of one of the Pb contaminants.

(3) The data define a linear trend with at least moderately good correlation with As contents. A single source for Pb and As contamination would be suggested. The y-axis intercept of the mixing trend defines the $^{206}Pb/^{204}Pb$ of the Pb and As contaminant in this soil.

Answers to Specific Questions Posed by USEPA

Question 1. Do the isotopic ratios for lead in residential site soils depend on the level of either arsenic or lead present in the sample? If so, what are the characteristic ratios for high-lead or arsenic samples compared to low-lead or arsenic samples?

Answer. Soils with high Pb contents show isotopic values that span the entire range of those observed within the soils with $^{206}Pb/^{204}Pb \approx 17.8\text{-}18.8$. Low-Pb soils show a much more restricted range with $^{206}Pb/^{204}Pb \approx 18.3\text{-}18.5$.

Four of six high-As samples have $^{206}Pb/^{204}Pb < 18.0$ whereas two other high-As samples have $^{206}Pb/^{204}Pb \approx 18.1\text{-}18.2$. All high-As samples analyzed are also high in Pb.

With two exceptions (both from the same residential property), low As soils are characterized by $^{206}Pb/^{204}Pb > 18.3$.

Question 2. Do the isotopic ratios observed in residential site soils resemble one or more of the potential source materials (Globe soils, PAX, lead arsenate pesticide)? If so, how does this depend on lead or arsenic level in the residential soil?

Answer. Four of six high-As samples have lower $^{206}Pb/^{204}Pb$ than found in any of the identified contaminants except PAX. Two high-As samples have $^{206}Pb/^{204}Pb$ similar to smelter material and Acme lead arsenate. Low-As and low-Pb soils have Pb isotopic values similar to baseline values.

Question 3. Does this approach allow you to identify one or more of the potential source materials as being more likely for the observed contamination in site soils than the other potential source materials?

Answer. Four of six high-As samples must have some PAX or isotopically similar material within them. Specific sources could not be identified for the other two high-As samples. The presence of smelter material or Acme lead arsenate is neither required nor eliminated by the Pb isotopic data in any of the soils.

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Appendix 1. Standard analytical procedures for lead isotopic analyses (nitric acid-hydrogen peroxide digestion) of metal-rich samples.

A. Acid digestion

    1. Samples are digested in accordance with Section 7.2 of method 3050B, EPA SW 846, revision 2 (12/96), with minor modifications to accommodate smaller sample sizes. Although the Pb isotopic analyses would require sample sizes of only a few milligrams for most samples, sample sizes of approximately 50 mg to 200 mg are digested in order to ensure that they are representative of the bulk sample.

    2. 2 to 3 ml of 1:1 nitric acid (HNO_3) are added to the sample in a PFA-teflon, screw-cap container. The sample is heated to near boiling for 15 minutes in the closed container. The sample is allowed to cool, and 1ml of concentrated HNO_3 is added. If brown fumes are observed, another 1 ml of HNO_3 is added and the procedure repeated until fuming is no longer observed. The solution is then heated to near boiling for approximately 2 hours in the closed container.

    3. The sample is allowed to cool and 1 ml of water and 1 ml of 30% hydrogen peroxide (H_2O_2) are added to the sample. Additional H_2O_2 is added in 0.1-ml increments until either strong effervescence subsides or until the general sample appearance remains unchanged.

    4. The sample is heated to just below boiling for approximately two hours in the closed container.

    5. The sample is allowed to cool and is diluted to 15 ml with deionized water. The sample is centrifuged and the supernatant transferred to an HDPE bottle.

    6. A lead blank of 0.3 ng (10^{-9} g) was obtained for this procedure.

B. Ion Exchange Chromatography

    1. An aliquot of the solution, corresponding to approximately 0.5 ug of Pb based on preliminary estimates of the Pb concentration provided by the submitter, is transferred to a teflon beaker and evaporated to dryness

    2. 1-2 ml of 6M hydrochloric acid (HCl) is added to the sample and again evaporated to dryness. Then 0.5-1 ml of 1.0-1.2 N hydrobromic acid (HBr) is added to the sample and is warmed gently for 5-10 minutes.

    3. The sample is allowed to cool, centrifuged, and the supernatant is loaded onto an anion-exchange column (0.8-1.0 ml resin volume) using Dowex AG1-X8 anion exchange resin.

    4. The column is washed with 1.0-1.2N HBr and water.

5. The Pb is eluted from the column with 6-8N HCl.

6. The sample is evaporated to dryness and ≈0.25 ml of 1.2N HBr is added.

7. The sample is loaded onto a second anion exchange column (AG1-X8 resin) with a resin volume of 0.1-0.2 ml.

8. The column is washed with 1.0-1.2N HBr and water.

9. Lead is eluted from the column with dilute (≤1M) Nitric Acid.

10. 2-3 drops of dilute (0.25-0.5%) phosphoric acid are added to the sample and it is evaporated to dryness.

11. Samples are then ready to be loaded onto filaments for mass spectrometry.

12. A Pb blank of 0.09 ng was obtained for this procedure.

C. Mass spectrometry

Data for samples and standards run during this study were acquired using the following procedure:

1. Aliquots of the samples were loaded onto rhenium filaments with colloidal silica gel and loaded into the mass spectrometer. Sample filaments were heated to 2.3-2.4 amp.

   a. During the initial stages of the study approximately 1/3 of the sample was loaded onto the filament. However, this produced an ion-beam intensity of $>10^{-10}$ Amp for ^{208}Pb, the maximum measurable signal. Consequently, approximately 1/2-1/3 of this amount was loaded for subsequent analyses.

2. The temperature of the filament was adjusted to 1250°C ± 5% (1187-1313°C).

   a. The temperature was determined by the data-acquisition software from a pyrometer supplied with the mass spectrometer. These temperatures may be ≈ 120°C lower than the true filament temperatures as determined by other pyrometers.

3. The beam was centered and focussed using the most intense peak, ^{208}Pb. In most instances the initial current was less than 1250°C so that samples were run at the lower end of the temperature window. In many instances, a ^{208}Pb intensity of $>10^{-10}$ amp, the maximum signal allowed, was obtained. The filament current was then decreased until appropriate beam intensity was achieved.

4. Isotopic data for all samples and standards are obtained using "L1, H1, H2, and H3" collectors for ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively. Data are acquired in "static" mode using on line software designed by the manufacturer. Each run consisted of 4

blocks of 12 data cycles. All peaks in each data cycle are measured simultaneously with 5 to 8 one-second integrations per cycle. Baselines at the half-mass positions are measured at the beginning and end of each block. The software provided by the manufacturer (Sector 54-relase 3.974) calculates a running average and statistical data.

Appendix 2. Quality Assurance and Quality Control (QA and QC)

Reagent Preparations and Analytical Blanks

Nitric, Hydrochloric and Hydrobromic acids are purified by sub-boiling distillation within the analyst's laboratory from commercially available reagent grade acids. Dilute acids are prepared by titration of the distilled concentrated acid followed by dilution with the appropriate calculated amount of deionized water for the desired final concentration.

Deionized water is prepared from filtered tap water by passing it through two mixed-bed resin filters, an activated charcoal filter, and a "Milli-Q plus" commercial deionizing system. Measured Pb blanks for the purified acids and water are typically in the range of 0.001-0.01 ppb (10^{-9} g/ g).

Phosphoric acid is diluted from commercial analytical grade acid with deionized water. Hydrogen peroxide is commercial reagent grade material. Ion-exchange resin is commercially available analytical grade anion exchange resin

Reagents are considered acceptable if the overall chemical procedure blank is less than the amount required to alter the lead isotopic composition ($^{206}Pb/^{204}Pb$) of the sample by more than the maximum allowable 1 sigma-mean (0.05%). If the total blank exceeds specifications, then work is halted and each of the component reagents is checked to determine the source of Pb in the blank. Samples processed with the unacceptable blank are discarded and the analyses repeated when the problem has been corrected. Data obtained from samples run under conditions of an unacceptable blank are deemed unusable.

The maximum allowable blank is calculated based on the Pb isotopic differences between the samples and the blank. The maximum blank is calculated to be that amount which when added to the sample will change the isotopic composition of the sample by no more than the target 1 sigma-mean precision. For example, the target precision for $^{206}Pb/^{204}Pb$ is 0.05%. If the sample $^{206}Pb/^{204}Pb$ were 17.0, then the maximum blank contribution would have no more than a 0.05% effect on the $^{206}Pb/^{204}Pb$ of the sample, or an effect of 0.0085 absolute. With a blank $^{206}Pb/^{204}Pb$ of 19.0, the maximum Pb mass allowable in the blank for 0.5 ug of sample lead can be calculated in the following manner:

$$(0.5*17.0+X*19.0)/(0.5+X) = 17.0085$$

Where x is the maximum blank in ug.

Solving for x = 0.0021ug (2.1 ng) or 0.4% of the sample Pb. If the $^{206}Pb/^{204}Pb$ of the sample is closer to that of the blank, then the maximum allowable blank increases, for example to 4.5ng for a sample $^{206}Pb/^{204}Pb$ = 18.0.

Because samples were aliquotted after acid-hydrogen peroxide digestion, it is necessary to evaluate the Pb blank in both the digestion procedure and the total chemical procedure in order to ensure that the Pb blank does not exceed specifications at any stage of the overall procedure. A Pb blank of 0.3 ng (10^{-9}g) was obtained for the acid and hydrogen peroxide digestion procedure (procedure "A" in Appendix 1). The minimum amount of Pb present in any of the acid digestions (sample 3-15644-B) was approximately 9 ug. Thus the blank contribution was less than 0.004%.

A total-chemistry blank was processed in the same manner as the samples. A 1-ml aliquot from the digestion procedure was processed through ion-exchange chemistry (procedure "B" in Appendix 1). Therefore, this blank is a measure of both the Pb contributions from the acid digestion to a sample aliquot as well as the subsequent chemical procedures applied to the aliquot. A total-chemistry blank of 0.09 ng was obtained. The average amount of sample lead processed through chemistry was 0.5 ug so that the blank contribution was less than 0.02%. Consequently both blanks were well within specifications and no blank correction was applied to the isotopic data.

Mass Spectrometry Calibrations.

Pb isotopic data are acquired using a VG-Sector 54, 7-collector, thermal ionization mass spectrometer. Up to twenty samples may be loaded into the mass spectrometer at a time. The positions of the individual samples on the turret are recorded in the mass spectrometer logbook and the software supplied by the manufacturer keeps track of the turret. A turret of samples will normally consist of at least two primary standards (NIST SRM-981) which are used to monitor mass fractionation induced by the mass spectrometry, a second primary standard (NIST SRM 982), and seventeen unknown samples. Data are collected using "static" mode (each isotope is measured simultaneously on a separate collector). At least one SRM 981 standard is run at the beginning, and the other at the end of the analyses of the unknowns.

At the beginning of each group of analyses or daily when a set of analyses requires more than one day to complete, the collector gains are calibrated using a computerized sub-routine supplied by the manufacturer of the Mass Spectrometer.

Should the gain calibrations not be of acceptable precision based on print out from the calibration sub-routine, the following steps are taken: (1) the calibration is repeated. (2) If the second calibration also fails, the electronics to the mass spectrometer are shut off, and the software rebooted. The electronics are then turned back on and the calibration repeated. (3) If

the third calibration also fails, step (2) is repeated. (4) If the 4th calibration fails, then all work is stopped until a qualified electronics technician is able to examine and correct the problem.

Mass Spectrometry Standards

Analyses of NIST standard SRM 981 (Cantanzaro and others, 1968; Todt and others, 1993) are used to monitor mass fractionation during mass spectrometry. At least two standards are loaded into the mass spectrometer for each batch of samples (at least 10% of the runs are primary standards). Analyses of NIST standard SRM 982 (Cantanzaro and others, 1968; Todt and others, 1993) are also used to check the mass fractionation corrections (at least 1 in 20 or 5%).

Data are acquired at filament temperatures of approximately 1150-1350C, as determined by the pyrometer supplied with the mass spectrometer (Unruh and others, 2000). Data are considered acceptable if the standard error (one sigma mean based on the total number of cycles) is better than $\pm$ 0.05% for $^{206}Pb/^{204}Pb$, and better than $\pm0.02\%$ for $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ as determined by the on-line data reduction program provided by the manufacturer of the mass spectrometer.

The principal source of analytical uncertainty in mass spectrometric measurements of Pb isotopes is mass fractionation induced during mass spectrometry. Lighter-mass isotopes are more efficiently evaporated from the filament and transported down the flight tube to the detector. Consequently, the measured isotopic ratio of a heavier mass to a lighter mass (e.g. $^{206}Pb/^{204}Pb$) will generally be slightly lower than the true value. Standards with certified isotopic compositions are run so that mass fractionation effects may be determined. Corrections to the isotopic ratios of the sample data are made based on the amount of mass fractionation determined from the analyses of the standards.

Results for twenty-three analyses of NIST standard SRM 981 are summarized in Table A2-1. Apparent mass fractionation factors are calculated for three isotope ratios, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, and $^{208}Pb/^{206}Pb$ using a linear mass fractionation law as follows (e.g. Ludwig, 1980):

$$F_a = [(R_t / R_a)-1]\ *100\ /\ \Delta M$$

Where F_a is the fractionation factor in percent per AMU for a given isotopic ratio, R_a is the measured ratio, R_t is the true ratio, and ΔM is the nominal mass difference between the two isotopes (2 for $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$, and 1 for $^{207}Pb/^{206}Pb$). The calculated fractionation

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Table A2-1. Lead Isotopic analyses of NIST standard SRM 981

Sample	Temp	$^{206}Pb/^{204}Pb$[1]	% S.E.	$^{207}Pb/^{204}Pb$[1]	% S.E.	$^{208}Pb/^{204}Pb$[1]	% S.E.	$F^{206}Pb/^{204}Pb$[2]	$F^{207}Pb/^{204}Pb$[2]	$F^{208}Pb/^{204}Pb$[2]
Certified Values[3]		16.9370	0.0630	0.914640	0.0360	2.16810	0.0370			
Redetermined Values[4]		16.9322	0.0047	0.914561	0.0044	2.16662	0.0060			
SRM 981-1	1123	16.8981	0.0016	0.913672	0.0006	2.16241	0.0009	0.101 ± 0.001	0.097 ± 0.001	0.097 ± 0.000
SRM 981-2	1118	16.8994	0.0015	0.913717	0.0021	2.16243	0.0010	0.097 ± 0.001	0.092 ± 0.002	0.097 ± 0.002
SRM 981-3	1218	16.9147	0.0064	0.913691	0.0020	2.16390	0.0039	0.052 ± 0.003	0.073 ± 0.006	0.063 ± 0.002
SRM 981-4	1192	16.9118	0.0022	0.914069	0.0008	2.16418	0.0012	0.060 ± 0.001	0.054 ± 0.001	0.056 ± 0.001
SRM 981-5	1192	16.9051	0.0031	0.913902	0.0009	2.16341	0.0023	0.080 ± 0.002	0.072 ± 0.001	0.074 ± 0.001
SRM 981-6	1190	16.9093	0.0046	0.913942	0.0014	2.16400	0.0033	0.068 ± 0.002	0.068 ± 0.001	0.061 ± 0.002
SRM 981-7	1190	16.8991	0.0028	0.913753	0.0011	2.16281	0.0023	0.098 ± 0.001	0.088 ± 0.001	0.088 ± 0.001
SRM 981-8	1168	16.8988	0.0024	0.913724	0.0007	2.16280	0.0014	0.099 ± 0.001	0.092 ± 0.001	0.088 ± 0.001
SRM 981-9	1163	16.9009	0.0037	0.913732	0.0014	2.16282	0.0031	0.093 ± 0.002	0.091 ± 0.001	0.088 ± 0.002
SRM 981-9	1206	16.9167	0.0044	0.914124	0.0013	2.16495	0.0032	0.046 ± 0.002	0.048 ± 0.001	0.039 ± 0.002
SRM 981-10	1151	16.9007	0.0025	0.913750	0.0008	2.16277	0.0012	0.093 ± 0.001	0.089 ± 0.001	0.089 ± 0.001
SRM 981-10	1210	16.9165	0.0022	0.914118	0.0007	2.16474	0.0013	0.046 ± 0.001	0.048 ± 0.001	0.043 ± 0.001
SRM 981-11	1179	16.9038	0.0021	0.913827	0.0011	2.16320	0.0021	0.084 ± 0.001	0.080 ± 0.001	0.079 ± 0.001
SRM 981-11	1174	16.9045	0.0035	0.913817	0.0008	2.16318	0.0007	0.082 ± 0.002	0.081 ± 0.001	0.080 ± 0.000
SRM 981-12	1186	16.9049	0.0035	0.913808	0.0017	2.16314	0.0033	0.081 ± 0.002	0.082 ± 0.002	0.080 ± 0.002
SRM 981-12	1230	16.9265	0.0045	0.914329	0.0020	2.16560	0.0039	0.017 ± 0.002	0.025 ± 0.002	0.019 ± 0.002
SRM 981-13	1113	16.8910	0.0042	0.913649	0.0010	2.16190	0.0013	0.122 ± 0.002	0.100 ± 0.001	0.109 ± 0.001
SRM 981-13	1185	16.9040	0.0032	0.913857	0.0009	2.16322	0.0016	0.083 ± 0.002	0.077 ± 0.001	0.079 ± 0.001
SRM 981-14	1195	16.8919	0.0042	0.913506	0.0017	2.16148	0.0030	0.119 ± 0.002	0.115 ± 0.002	0.119 ± 0.002
SRM 981-15	1136	16.8854	0.0033	0.913242	0.0011	2.16407	0.0017	0.139 ± 0.002	0.144 ± 0.001	0.059 ± 0.001
SRM 981-16	1315	16.9230	0.0069	0.914055	0.0022	2.16517	0.0063	0.027 ± 0.004	0.055 ± 0.002	0.033 ± 0.003
SRM 981-17	1234	16.9185	0.0133	0.913869	0.0036	2.16381	0.0058	0.040 ± 0.007	0.076 ± 0.004	0.065 ± 0.003
SRM 981-20	1238	16.9102	0.0064	0.914049	0.0020	2.16435	0.0046	0.065 ± 0.003	0.056 ± 0.002	0.052 ± 0.002
SRM 981-21	1198	16.9031	0.0028	0.913921	0.0013	2.16343	0.0028	0.086 ± 0.001	0.070 ± 0.001	0.074 ± 0.001
SRM 981-22	1216	16.9034	0.0039	0.913867	0.0017	2.16326	0.0032	0.085 ± 0.002	0.076 ± 0.002	0.076 ± 0.002
SRM 981-23	1212	16.9013	0.0067	0.913771	0.0018	2.16294	0.0034	0.091 ± 0.003	0.086 ± 0.002	0.085 ± 0.002
SRM 981-24	1190	16.9015	0.0023	0.913786	0.0005	2.16302	0.0006	0.091 ± 0.001	0.085 ± 0.001	0.085 ± 0.001
SRM 981-25	1197	16.8954	0.0024	0.913513	0.0010	2.16186	0.0011	0.109 ± 0.001	0.115 ± 0.001	0.110 ± 0.001
MEAN, ALL[5]	N=28	16.9048	0.0570	0.913830	0.0230	2.16326	0.0470	0.081 ± 0.029	0.080 ± 0.023	0.078 ± 0.024
MEAN, T<1140[5]	N=4	16.8935	0.0460	0.913570	0.0250	2.16180	0.0540	0.115 ± 0.023	0.106 ± 0.025	0.111 ± 0.027
MEAN, T>1220[5]	N=4	16.9200	0.0570	0.914080	0.0260	2.16480	0.0570	0.036 ± 0.029	0.053 ± 0.026	0.042 ± 0.029
MEAN, T = 1140-1220[5]	N=20	16.9043	0.0440	0.913833	0.0210	2.16325	0.0420	0.083 ± 0.022	0.080 ± 0.021	0.078 ± 0.021
Correction factors[6]								0.166 ± 0.044	0.080 ± 0.021	0.156 ± 0.042
MEAN T = 1140-1220[7]	N=20	16.9043	0.0440	0.913833	0.0210	2.16325	0.0420	0.097 ± 0.022	0.086 ± 0.021	0.112 ± 0.021

Runs for samples received 04/01-05/01

Sample	Temp									
981-24-VB137	1190	16.9015	0.0023	0.913786	0.0005	2.16302	0.0006	0.091 ± 0.001	0.085 ± 0.001	0.083 ± 0.000
981-25-VB139	1197	16.8954	0.0024	0.913513	0.0010	2.16186	0.0011	0.109 ± 0.001	0.115 ± 0.001	0.110 ± 0.001
981-26-VB140	1168	16.9039	0.0036	0.913899	0.0014	2.16207	0.0141	0.084 ± 0.002	0.072 ± 0.001	0.105 ± 0.007
981-26-VB140	1143	16.9109	0.0038	0.914072	0.0009	2.16425	0.0007	0.063 ± 0.002	0.053 ± 0.001	0.055 ± 0.000
981-27-VB158	1145	16.9019	0.0069	0.913814	0.0024	2.16321	0.0049	0.090 ± 0.003	0.082 ± 0.002	0.079 ± 0.002

Table A2-1, Cont'd.

Sample	Temp	^{206}Pb/^{204}Pb[1]	% S.E.	^{207}Pb/^{204}Pb[1]	% S.E.	^{208}Pb/^{204}Pb[1]	% S.E.	F ^{206}Pb/^{204}Pb[2]	F ^{207}Pb/^{204}Pb[2]	F ^{208}Pb/^{204}Pb[2]
981-28-VB160	1166	16.9034	0.0022	0.913757	0.0008	2.16302	0.0014	0.085 ± 0.001	0.088 ± 0.001	0.083 ± 0.001
981-29-VB178	1091	16.9045	0.0019	0.913759	0.0006	2.16244	0.0009	0.082 ± 0.001	0.088 ± 0.001	0.097 ± 0.000
981-29-VB178	1166	16.9106	0.0031	0.914159	0.0016	2.16354	0.0030	0.064 ± 0.002	0.044 ± 0.002	0.071 ± 0.002
981-30-VB180	1157	16.9071	0.0039	0.913788	0.0017	2.16306	0.0031	0.074 ± 0.002	0.085 ± 0.002	0.082 ± 0.002
981-31-VB190	1165	16.9114	0.0029	0.913994	0.0006	2.16374	0.0005	0.061 ± 0.001	0.062 ± 0.001	0.067 ± 0.000
MEAN, ALL[5]	N = 10	16.9051	0.0300	0.913850	0.0200	2.16302	0.0340	0.080 ± 0.015	0.078 ± 0.020	0.083 ± 0.017
MEAN, T = 1140-1220[5]	N = 9	16.9051	0.0310	0.913860	0.0210	2.16309	0.0350	**0.080 ± 0.016**	**0.077 ± 0.021**	**0.082 ± 0.018**
Correction factors[6]								**0.160 ± 0.032**	**0.077 ± 0.021**	**0.164 ± 0.036**
MEAN T = 1140-1220[7]	N = 9	16.9051	0.0310	0.913860	0.0210	2.16309		0.094 ± 0.015	0.085 ± 0.020	0.116 ± 0.017

[1] Uncertainties are 1 standard error (1 S.E.~ 1 sigma mean) in percent.

[2] Calculated fractionation factors in percent per AMU for each ratio, uncertainties are at 1 S.E. in percent. Calculations are relative to the redermined values of Todt and others, 1993, unless otherwise noted.

[3] Certified values from Cantanzaro and others, 1968.

[4] Redetermined values from Todt and others, 1993.

[5] Uncertainties correspond to 1 sigma. Preferred values shown in bold.

[6] mass fractionation correction factors applied to sample isotopic ratios.

[7] Calculated relative to the values of Cantanzaro and others, 1968. Uncertainties are 1 sigma.

factors also account for small possible differences in collector efficiencies and are therefore calculated separately for each isotope ratio.

The amount of mass fractionation for a given run is a function of several variables including filament thickness; relative amounts of Pb, phosphoric acid, and silica gel; the particle size of the silica gel; and the filament temperature during data acquisition. Although the calculated fractionation factors do appear to vary with temperature (Table A2-1), the relationships are not particularly well correlated ($r^2 \leq 0.6$). Consequently, no attempt was made to "fine tune" the calculations as a function of running temperature. Instead, a temperature interval of approximately 1140°C-1220°C was selected to represent acceptable running conditions.

This temperature interval shows reasonably consistent calculated fractionation factors, and encompasses the bulk of the standard runs (mean values in bold type in Table A2-1). Data were accepted for only those samples that were also run within this temperature interval.

Mean calculated fractionation factors are shown relative to both the original certified values for NIST standard SRM-981 (Cantanzaro and others, 1968) and to the more precise redetermined values of Todt and others (1993). The calculated fractionation factors relative to the redetermined standard values are more internally consistent than those relative to the original values. Consequently, the factors calculated relative to the redetermined values were used to correct the sample data.

As a test of the correction procedures, twelve samples of NIST standard SRM-982 were run. Fractionation factors for each isotope ratio for each SRM 982 standard run have been calculated in the manner outlined above. Fractionation factors for the means of the twelve analyses have been calculated relative to both the original certified values (Cantanzaro and others, 1968) and the redetermined values (Todt and others, 1993). The results relative to the original certified values are more internally consistent (bold line in Table A2-2). Agreement between the standards is within 0.011% per AMU for $^{207}Pb/^{206}Pb$, 0.016% per AMU for $^{208}Pb/^{206}Pb$, and 0.033% per AMU for $^{206}Pb/^{204}Pb$.

Data Reduction

Raw Data are corrected for mass fractionation based on the analyses of the SRM 981 standards (Table A2-1) using the following equation (Ludwig, 1980):

$$R_c = R_a * (1 + \Delta M * F_a/100)$$

Table A2-2. Lead Isotopic analyses of NIST standard SRM 982

Sample	Temp	$^{206}Pb/^{204}Pb$[1]	% S.E.	$^{207}Pb/^{206}Pb$[1]	% S.E.	$^{208}Pb/^{206}Pb$[1]	% S.E.	$F\ ^{206}Pb/^{204}Pb$[2]	$F\ ^{208}Pb/^{204}Pb$[2]	$F\ ^{208}Pb/^{204}Pb$[2]
Certified Values[3]		36.7390	0.0990	0.467070	0.0430	1.00016	0.0360			
Redetermined Values[4]		36.7537	0.0027	0.467003	0.0011	1.00016	**[4]			
SRM 982-1	1144	36.6569	0.0021	0.466533	0.0006	0.99792	0.0011	0.112 ± 0.001	0.115 ± 0.001	0.112 ± 0.001
SRM 982-2	1207	36.6500	0.0041	0.466571	0.0017	0.99793	0.0023	0.121 ± 0.002	0.107 ± 0.002	0.112 ± 0.001
SRM 982-3	1194	36.6676	0.0020	0.466648	0.0006	0.99842	0.0014	0.097 ± 0.001	0.090 ± 0.001	0.087 ± 0.001
SRM 982-4	1166	36.6427	0.0039	0.466530	0.0016	0.99787	0.0036	0.131 ± 0.002	0.116 ± 0.002	0.115 ± 0.002
SRM 982-5	1195	36.6564	0.0050	0.466643	0.0019	0.99833	0.0042	0.113 ± 0.003	0.092 ± 0.002	0.092 ± 0.002
SRM 982-6	1206	36.6668	0.0048	0.466686	0.0018	0.99857	0.0040	0.098 ± 0.002	0.082 ± 0.002	0.080 ± 0.002
SRM 982-7	1192	36.6498	0.0054	0.466658	0.0012	0.99831	0.0020	0.122 ± 0.003	0.088 ± 0.001	0.093 ± 0.001
SRM 982-8	1215	36.6302	0.0106	0.466778	0.0015	0.99855	0.0024	0.149 ± 0.005	0.063 ± 0.002	0.081 ± 0.001
SRM 982-9	1222	36.6699	0.0031	0.466712	0.0013	0.99863	0.0026	0.094 ± 0.002	0.077 ± 0.001	0.077 ± 0.001
SRM 982-10	1193	36.6460	0.0030	0.466624	0.0011	0.99812	0.0021	0.127 ± 0.002	0.096 ± 0.001	0.102 ± 0.001
SRM 982-11	1197	36.6637	0.0028	0.466734	0.0006	0.99863	0.0007	0.103 ± 0.001	0.072 ± 0.001	0.076 ± 0.000
SRM 982-12	1197	36.6457	0.0027	0.466628	0.0011	0.99818	0.0026	0.127 ± 0.001	0.095 ± 0.001	0.099 ± 0.001
SRM 982-13	1165	36.6471	0.0032	0.466542	0.0009	0.99789	0.0021	0.125 ± 0.002	0.113 ± 0.001	0.114 ± 0.001
SRM 982-14	1170	36.6381	0.0028	0.466487	0.0009	0.99759	0.0016	0.138 ± 0.001	0.125 ± 0.001	0.129 ± 0.001
SRM 982-15	1166	36.6660	0.0023	0.466680	0.0010	0.99845	0.0020	0.100 ± 0.001	0.084 ± 0.001	0.086 ± 0.001
SRM 982-16	1150	36.6687	0.0035	0.466653	0.0013	0.99831	0.0027	0.096 ± 0.002	0.089 ± 0.001	0.093 ± 0.001
SRM 982-17	1186	36.6663	0.0031	0.466617	0.0012	0.99824	0.0024	0.099 ± 0.002	0.097 ± 0.001	0.096 ± 0.001
Mean[5]		36.6549	0.0330	0.466631	0.0170	0.99823	0.0320	**0.115 ± 0.017**	**0.094 ± 0.017**	**0.097 ± 0.016**
Mean[6]		36.6549	0.0330	0.466631	0.0170	0.99823	0.0320	0.135 ± 0.017	0.080 ± 0.017	0.097 ± 0.016

[1] Uncertainties are 1 standard error (1 S.E. = 1 sigma mean) in percent.

[2] Calculated fractionation factors in percent per AMU for each ratio, uncertainties are at 1 S.E. in percent. Calculations are relative to the certified values of Cantanzaro and others, 1968, unless otherwise noted.

[3] Certified values from Cantanzaro and others, 1968.

[4] Redetermined values from Todt and others, 1993. Calculations based on an assumed $^{208}Pb/^{206}Pb$ = 1.00016.

[5] Preferred values shown in bold. Uncertainties correspond to 1 sigma.

[6] Calculated relative to the values of Todt and others, 1993. Uncertainties are 1 sigma.

Where R_c is the corrected ratio, R_a is the measured ratio, F_a is the calculated fractionation factor as defined above, and ΔM is the nominal mass difference between the numerator and denominator isotopes. Both the F_a values and the correction factors ($= \Delta M * F_a$) for each isotope ratio are shown in bold type in Table A2-1. Also shown are the 1-sigma uncertainties for both sets of values.

Precision for the mass fractionation-corrected data for individual mass spectrometry runs listed in Table 2 is calculated at the 95% confidence interval (C.I.) using the equations given by Ludwig (1980; 1994) with the following parameters: 3.2 times the measured standard error (based on 4 blocks of data in each run) and the 2.05 times the 1-sigma uncertainty from the average of the SRM-981 standard runs (Table A2-1; based on 20 runs). Weighted means and uncertainties for data from individual samples are then calculated from the data for individual runs also at the 95% C.I.

Replicate Analyses

Three types of replicate samples were analyzed. (1) Blind duplicates were submitted by USEPA. (2) Replicate acid-hydrogen peroxide digestions of the same sample were performed in order to evaluate sample homogeneity as well as the reproducibility of the digestion procedure (digestion replicates). These are designated by different suffix letters in Tables 1 and A2-4 (e.g. 642B-A, 642B-B, 642B-C). (3) Replicate loads of the same sample from a single chemical procedure (mass spectrometry replicates) were run in order to evaluate the reproducibility of the mass spectrometric procedures. These replicates are designated by separate entries under a single sample number in Tables 2 and A2-3.

Two sets of blind duplicates were submitted by USEPA. These were the baseline soil, samples 3-15653-B and 3-15654-B (EPA number SC-000650), and high-As-focal samples 3-15650-B and 3-15651-B (EPA number SC-00046). Results for the duplicates of the baseline soil are in reasonably good agreement and in fact the variation between the two samples is less than that found among duplicate acid digestions of sample 3-15654-B (Table 2). Results for the duplicate analyses of the high-As-focal sample are in agreement within analytical uncertainty ($^{206}Pb/^{204}Pb = 17.801 \pm 0.009$ and 17.789 ± 0.009; Table 2).

Samples from most individual acid-digestions were run at least twice under acceptable temperature and beam-intensity conditions outlined above (Table 2). Data were corrected for mass fractionation and a weighted mean and uncertainty were calculated also as outlined above.

Table A2-3. Lead isotopic compositions from replicate runs of Sample 3-15642-B, Vasquez Blvd.-I70 Project

Sample/Lab No.[1]	Temp	$^{206}Pb/^{204}Pb^2$	$^{207}Pb/^{206}Pb^2$	$^{208}Pb/^{206}Pb^2$
3-15642-B				
642B-A	1078	18.1958 ± 0.0020%	0.85370 ± 0.0006%	2.08992 ± 0.0005%
642B-A	1188	18.2064 ± 0.0031%	0.85404 ± 0.0014%	2.09149 ± 0.0024%
642B-A	1167	18.2260 ± 0.0064%	0.85436 ± 0.0023%	2.09344 ± 0.0053%
642B-A	1194	18.2150 ± 0.0093%	0.85402 ± 0.0025%	2.09192 ± 0.0045%
642B-A	1273	18.1949 ± 0.0045%	0.85359 ± 0.0010%	2.08987 ± 0.0012%
642B-A	1213	18.2196 ± 0.0063%	0.85400 ± 0.0025%	2.09185 ± 0.0054%
642B-A	1191	18.2284 ± 0.0127%	0.85371 ± 0.0028%	2.09137 ± 0.0044%
Mean-All[3]		18.212 ± 0.075%	0.85392 ± 0.031%	2.0914 ± 0.059%
Mean-T=1140-1220[3]		18.219 ± 0.049%	0.85403 ± 0.027%	2.0920 ± 0.040%

[1] Data are for separate loads of a single processed aliquot of sample 3-15642-B

[2] Raw data uncorrected for mass fractionation. Corrected data are shown in Table 1.
   Uncertainties for individual runs are 1 standard error in % (1 S.E. ≈ 1 sigma mean)

[3] Uncertainties for means are 1 sigma in percent·

Table A2-4. Lead Isotopic data for replicate acid-digestions of selected soils samples from the Vasquez Blvd.-I70 Project.

Sample/Lab No[1]	Pb ppm[2]	Sample wt (g)	²⁰⁶Pb/²⁰⁴Pb[3]	²⁰⁷Pb/²⁰⁶Pb[3]	²⁰⁸Pb/²⁰⁶Pb[3]	²⁰⁷Pb/²⁰⁴Pb[3]	²⁰⁸Pb/²⁰⁴Pb[3]
3-15642-B	422						
Mean 642B-A		0.126	18.249 ± 0.007	0.85471 ± 0.00021	2.0953 ± 0.0008	15.596 ± 0.009	38.237 ± 0.029
Mean642B-B		0.072	18.219 ± 0.031	0.85570 ± 0.00065	2.0962 ± 0.0036	15.590 ± 0.039	38.191 ± 0.126
Mean642B-C		0.092	18.243 ± 0.009	0.85511 ± 0.00021	2.0960 ± 0.0010	15.600 ± 0.012	38.237 ± 0.036
Mean 642B A-C			18.242 ± 0.029	0.8551 ± 0.0009	2.0956 ± 0.0006	15.599 ± 0.007	38.235 ± 0.023
3-15644-B	39						
Mean 644B-A		0.233	18.452 ± 0.012	0.84521 ± 0.00025	2.0963 ± 0.0013	15.595 ± 0.014	38.681 ± 0.046
644B-B		0.255	18.497 ± 0.017	0.84213 ± 0.00036	2.0947 ± 0.0018	15.577 ± 0.021	38.746 ± 0.068
644B-C		0.191	18.610 ± 0.017	0.84048 ± 0.00037	2.1133 ± 0.0019	15.641 ± 0.021	39.326 ± 0.069
Mean 644B A-C			18.52 ± 0.20	0.8426 ± 0.0061	2.101 ± 0.023	15.604 ± 0.080	38.92 ± 0.90
3-15654-B	101						
Mean654B-A		0.254	18.869 ± 0.010	0.82794 ± 0.00021	2.0506 ± 0.0010	15.623 ± 0.012	38.693 ± 0.039
654B-B		0.177	18.459 ± 0.017	0.84513 ± 0.00037	2.0887 ± 0.0018	15.600 ± 0.021	38.556 ± 0.068
654B-C		0.164	18.454 ± 0.017	0.84637 ± 0.00037	2.0898 ± 0.0018	15.619 ± 0.021	38.564 ± 0.068
654B-D		0.078	18.496 ± 0.017	0.84416 ± 0.00036	2.0887 ± 0.0018	15.614 ± 0.021	38.633 ± 0.068
654B-E		0.272	18.385 ± 0.017	0.84836 ± 0.00037	2.0894 ± 0.0018	15.597 ± 0.021	38.414 ± 0.068
654B-F		0.219	18.460 ± 0.017	0.84461 ± 0.00036	2.0866 ± 0.0018	15.595 ± 0.021	38.554 ± 0.068
Mean 654B A-F			18.52 ± 0.18	0.8426 ± 0.0079	2.083 ± 0.016	15.610 ± 0.012	38.571 ± 0.097
Mean 654B B-F			18.451 ± 0.050	0.8456 ± 0.0020	2.0890 ± 0.0008	15.605 ± 0.009	38.544 ± 0.096
3-15655-B	151						
Mean 655B-A		0.260	18.297 ± 0.011	0.85249 ± 0.00026	2.0894 ± 0.0013	15.596 ± 0.014	38.231 ± 0.046
655B-B		0.152	18.312 ± 0.017	0.85129 ± 0.00037	2.0865 ± 0.0018	15.589 ± 0.021	38.209 ± 0.067
Mean 655B A-B			18.303 ± 0.073	0.8519 ± 0.0073	2.0880 ± 0.0173	15.595 ± 0.011	38.224 ± 0.037
3-15656-B	175						
Mean 656B-A		0.206	18.480 ± 0.010	0.84476 ± 0.0002	2.0711 ± 0.0018	15.611 ± 0.012	38.274 ± 0.038
656B-B		0.204	17.965 ± 0.016	0.86567 ± 0.00037	2.0975 ± 0.0018	15.569 ± 0.021	37.722 ± 0.067
656B-C		0.180	18.572 ± 0.017	0.84076 ± 0.00037	2.0722 ± 0.0018	15.614 ± 0.021	38.483 ± 0.068
656B-D		0.524	18.402 ± 0.017	0.84755 ± 0.00037	2.0726 ± 0.0018	15.597 ± 0.021	38.140 ± 0.067
656B-E		0.601	18.426 ± 0.017	0.84663 ± 0.00037	2.0705 ± 0.0018	15.600 ± 0.021	38.151 ± 0.067
Mean 656B A-E			18.37 ± 0.26	0.849 ± 0.011	2.077 ± 0.014	15.599 ± 0.021	38.16 ± 0.34
Mean 656B A, C-E			18.47 ± 0.12	0.8449 ± 0.004225	2.0714 ± 0.001	15.607 ± 0.006	39.26 ± 0.25
3-15657-B	1140						
Mean 657A		0.133	17.900 ± 0.011	0.86944 ± 0.00026	2.1125 ± 0.0013	15.563 ± 0.014	37.815 ± 0.045
657B-B		0.199	17.894 ± 0.016	0.87011 ± 0.00037	2.1135 ± 0.0018	15.570 ± 0.021	37.821 ± 0.067
Mean 657B A-B			17.898 ± 0.009	0.8698 ± 0.0040	2.1129 ± 0.0010	15.565 ± 0.011	37.817 ± 0.037
3-12152-B	1730						
Mean 152A		1.004	17.614 ± 0.006	0.8810 ± 0.0003	2.1198 ± 0.0011	15.517 ± 0.012	37.336 ± 0.035
Mean 152B		0.269	17.899 ± 0.006	0.8683 ± 0.0003	2.0997 ± 0.0010	15.542 ± 0.012	37.562 ± 0.035
Mean 152C		0.593	17.786 ± 0.006	0.8736 ± 0.0003	2.1064 ± 0.0011	15.537 ± 0.012	37.496 ± 0.035
Mean 152A-C			17.77 ± 0.36	0.874 ± 0.016	2.109 ± 0.025	15.532 ± 0.030	37.47 ± 0.31

1 Separate acid-digestions of the same sample are listed as "-A" through "-F". Only the mean values are shown when 2 or more
  mass spectrometer runs of the same subdample were obtained.
  Data are corrected for mass fractionation based on analyses of NIST standard SRM-981 (Table A2-1).
2 Pb concentrations provided by USEPA from acid digestions of splits of the samples.
3 Uncertainties are absolute and are at the 95% confidnece level (Ludwig, 1980; 1994).

Seven aliquots of one sample, 642B-A (3-15642-B), were run at a variety of temperatures as shown in Table A2-3. Mean values of all three isotope ratios were calculated for all data and only for those data run between approximately 1140°C and 1220°C as was done for the SRM 981 standard (Table A2-1). The calculated analytical uncertainties for the mean values are similar to those obtained for to those obtained for the mass fractionation correction factors calculated from analyses of the SRM 981 standard (Table A2-1).

Samples 3-15642-B (422 ppm Pb), 3-15644-B (39 ppm), 3-15654-B (110 ppm) and 3-12152-B (1730 ppm) were acid-digested in triplicate in order to evaluate the overall procedure and sample homogeneity. In addition, duplicate acid-digestions were performed on samples 3-15655-B (151 ppm), 3-15656-B (175 ppm), and 3-15657-B (1140 ppm). Significant isotopic variability was observed among samples 3-15654-B and 3-15656B, so three additional acid digestions of these two samples were performed (Table A2-4).

Two of the samples with moderate to high Pb content (3-15642-B, and 3-15657-B) show only minor variation in isotopic ratios among the data from replicate acid digestions (Table A2-4). In contrast, there is considerable isotopic variation observed among replicate acid-digestions of sample 3-12152-B.

Significant isotopic variation is observed among most of the samples with <200-ppm Pb. Data from one acid digestion of sample 3-15654-B show anomalously radiogenic Pb isotopic values whereas data for one from sample 3-15656-B show anomalously nonradiogenic values. Data for sample 3-15644-B also show rather large variation (0.85% in $^{206}Pb/^{204}Pb$). These variations are not related to mass fractionation corrections, but instead represent real variations induced either by the acid digestion procedures or as a result of sample heterogeneity.

Some isotopic heterogeneity within urban soils is perhaps to be expected. Soils at an individual site may be composed of a variety of natural and man made materials. The isotopic compositions of soils low in Pb are subject to influence by even small amounts of "exotic" material such as metal, solder, fertilizer, gasoline, etc. Such material may be randomly distributed at a given site and even within a given sample at that site. For example, inclusion of a single 0.0001 gram fragment of lead solder in a 1 gram sample of soil with 100 ppm Pb would effectively double the lead concentration in that 1-gram sample. The Pb isotopic composition would also be altered to the approximate average of that in the soil and that in the solder.

Samples higher in lead are generally much less sensitive to the effects of exotic materials. For example, the same 0.0001 gram fragment of solder in a 1 gram sample of soil 3-15657-B (1140 ppm) would alter the apparent Pb concentration by less than 10 percent

and would have only about one-fifth the effect on the lead isotopic composition as in the former case. Consequently, the variation in isotopic compositions observed among the replicate acid-digestions of sample 3-12152-B is somewhat more difficult to explain. The results may indicate that the high-Pb phase in this sample is very heterogeneously distributed within the soil. Alternatively the results may indicate that there is more than one contaminant in the soil and that they are either not uniformly distributed within the soil or that the acid-digestion procedure is not completely dissolving at least one of the contaminants.

The inclusion of small amounts of exotic material appears to be responsible for the atypical isotopic compositions of samples 654B-A (3-15654-B) and 656B-B (3-15656-B). The data for these two fractions is included in Pb isotopic variation diagrams (Figure 1), but are excluded from the mean calculations for the $^{206}Pb/^{204}Pb$ vs. Pb concentration diagram in Figure 2.

Method Determination Limit (Practical Quantitation Limit)

The method determination limit (MDL) is defined as the lowest analyte concentration that can be determined with a specified relative standard deviation (Vandecasteele and Block, 1993). For concentration measurements, the method determination limit is generally 3 to 5 times the detection limit (Vandecasteele and Block, 1993). EPA often refers to the method determination limit as the practical quantitation limit. In the case of isotopic measurements, where absolute concentrations are not measured, the definition is modified as the lowest ion-beam intensity at which a specified relative standard deviation is obtained. The chemical procedures employed prior to mass spectrometry are designed to produce a purified Pb fraction and thus to eliminate or at least minimize matrix effects. Consequently, the method determination limit is equivalent to the instrument determination limit. The method determination limit is defined as that intensity for ^{204}Pb (the least abundant isotope) below which the one-sigma-mean uncertainty in $^{206}Pb/^{204}Pb$ exceeds ±0.05%.

The method determination limit was determined as follows:

1. Seven aliquots of Pb standard solution (SRM-981) were loaded into the mass spectrometer and run using the normal software routine, but were repeatedly run at a variety of beam intensities.

2. Mean and standard errors (1 sigma mean) were calculated for the data from the seven runs at discreet beam intensity intervals.

3. The data were then plotted on a graph of relative standard deviation as a function of ^{204}Pb beam-intensity (Figure A2-1). Best-fit curves were calculated for each of the seven samples and the intensity at which the relative uncertainty equals 0.05% were calculated. The

method determination limit was then calculated from the mean of the seven samples as $3.7 \pm 0.2 \times 10^{-14}$ amps (Table A2-5, Figure A2-1). Beam intensities for normal running conditions are also shown in Figure A2-1 and are approximately one to two orders of magnitude larger than the MDL (2.5×10^{-13}A to 2.5×10^{-12} A).

Table A2-5. Summary of results for determination of the method determination limit (practical quantitation limit).

Standard Run	coeff. a[1]	coeff. b[1]	r^2 [2]	Minimum Intensity[3]
SRM981-38-00	-25.595	-0.86087	0.997	3.81×10^{-14}
SRM981-39-00	-30.038	-0.87641	0.995	3.98×10^{-14}
SRM981-40-00	-29.891	-0.87029	0.992	3.79×10^{-14}
SRM981-41-00	-29.364	-0.85108	0.988	3.50×10^{-14}
SRM981-42-00	-28.378	-0.81856	0.983	3.41×10^{-14}
SRM981-43-00	-29.213	-0.84817	0.996	3.77×10^{-14}
SRM981-44-00	-26.309	-0.75428	0.939	3.77×10^{-14}
MEAN = MDL				**$3.7 \pm 0.2 \times 10^{-14}$**

[1]Equations follow a power law in the form $Y = e^a * X^b$, where y is relative uncertainty and x is ^{204}Pb beam intensity in amps.

[2] r^2 is the regression correlation coefficient.

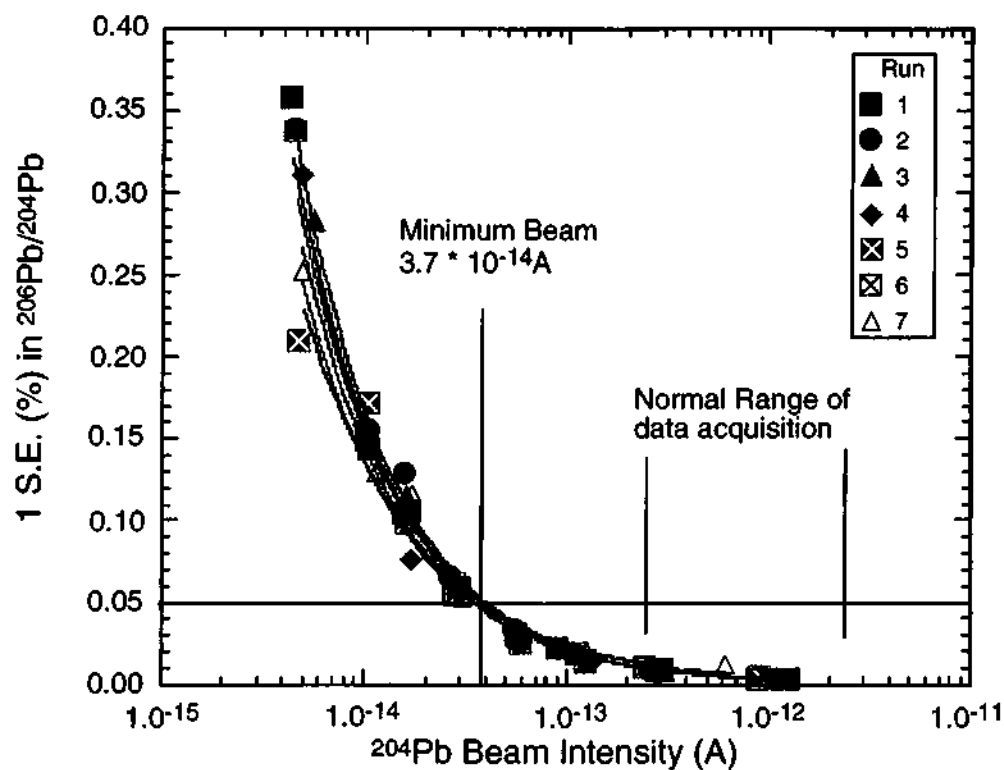[3] The minimum intensity in amps for each standard is calibrated for a 1 S.E. uncertainty of 0.05%.

0.40

0.35

0.30

0.25

0.20

0.15

0.10

0.05

0.00

1 S.E. (%) in $^{206}Pb/^{204}Pb$

Minimum Beam
3.7 * 10^{-14}A

Normal Range of
data acquisition

Run
1
2
3
4
5
6
7

1.0^{-15} 1.0^{-14} 1.0^{-13} 1.0^{-12} 1.0^{-11}

^{204}Pb Beam Intensity (A)

Figure A2-1. Percent Standard Error in $^{206}Pb/^{204}Pb$ vs. ^{204}Pb beam intensity for seven analyses of NIST standard SRM 981. Seven standards were run at a variety of beam intensities. Best-fit curves (unweighted) through data for each standard are show. The method determination limit (MDL) is defined as that ^{204}Pb beam intensity below which the 1S.E. for $^{206}Pb/^{204}Pb$ exceeds 0.05%.